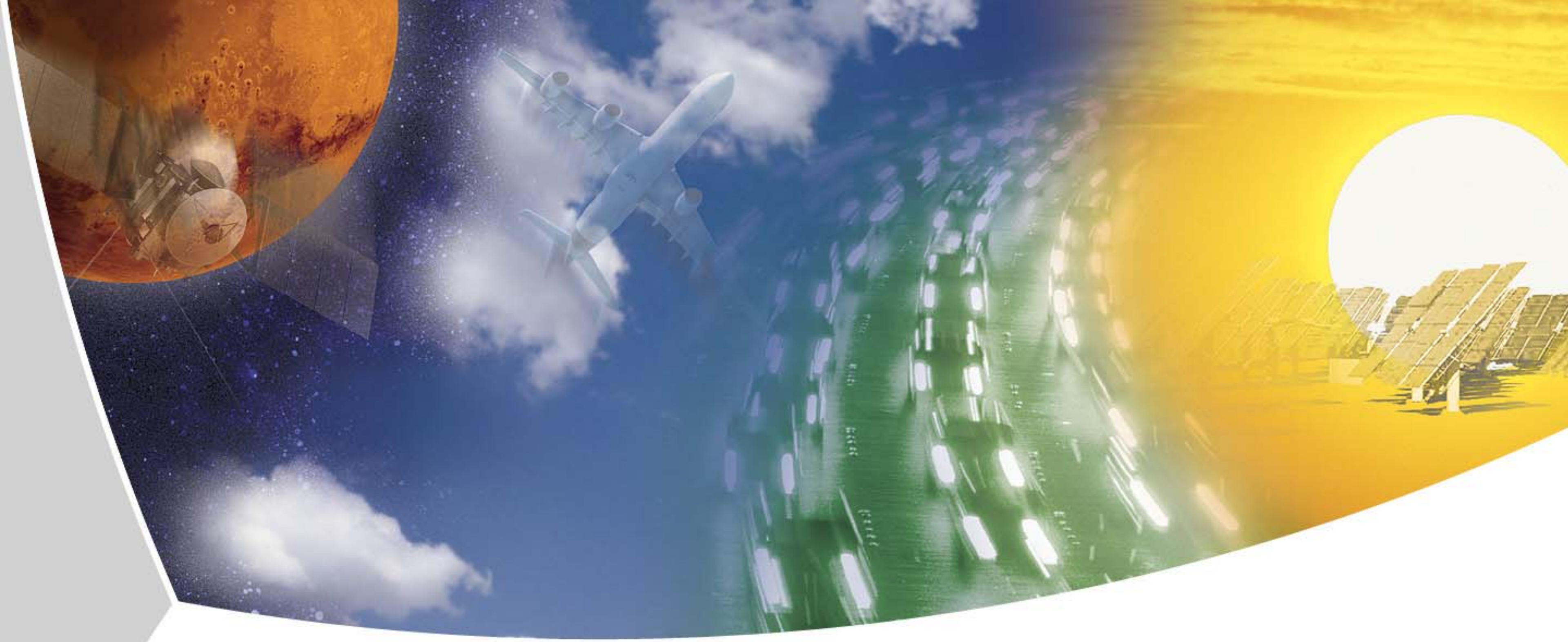


Application of Electrochemical Impedance Spectroscopy for Fuel Cell Characterization

Dr. Norbert Wagner
DLR, Institut für Technische Thermodynamik, Stuttgart

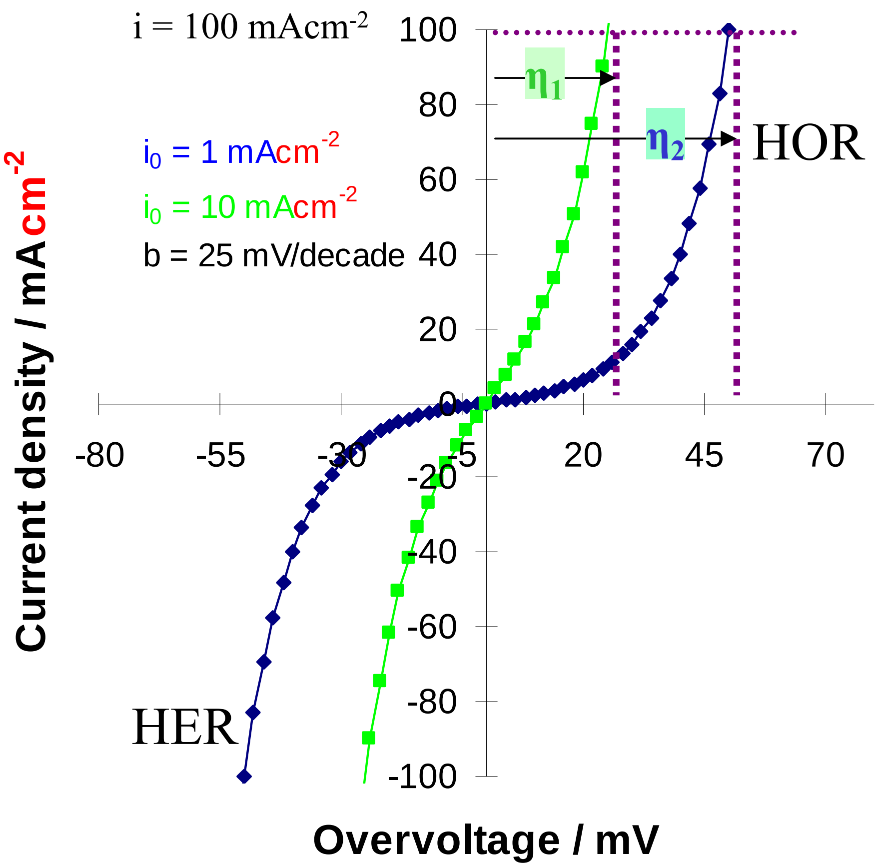
Kronach Impedance Days 2010
Kloster Banz, April, 14th – 16th , 2010

DLR Deutsches Zentrum für Luft- und Raumfahrt e.V.
in der Helmholtz-Gemeinschaft

Presentation outline

- Introduction and motivation
  - Examples of porous (technical) electrodes
- Theory and models of porous gas diffusion electrodes
  - Impedance models
- Application of Göhr‘s porous electrode model
  - EIS measured at PEFC
  - EIS measured during oxygen reduction on silver in alkaline solution
- Outlook
  - Experimental set up for EIS applied for stack measurements

Electrochemical kinetic and electrode structure



Butler-Volmer equation for hydrogen oxydation (HOR) and hydrogen evolution reaction (HER)

Increasing power output (P=I·U)
at constant cell voltage (overvoltage) by:

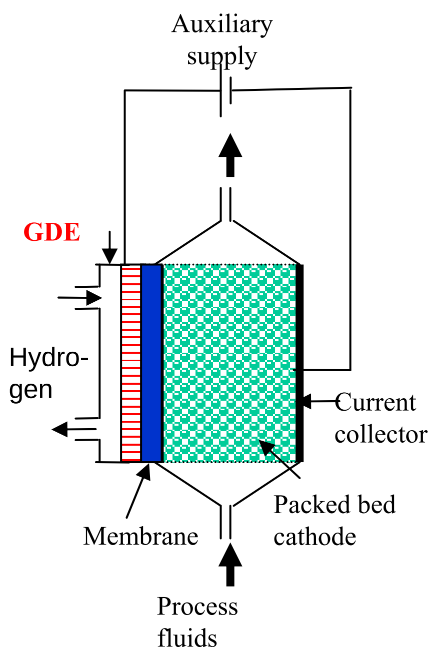
- enlargement of active electrode surface using porous electrodes (electrode structure)
- increasing i_0 (electrode material with high catalytic activity)

$$I = \text{Surface} \cdot i = \text{Surface} \cdot i_0 \cdot \exp\{(\alpha RT/zF)\eta\}$$

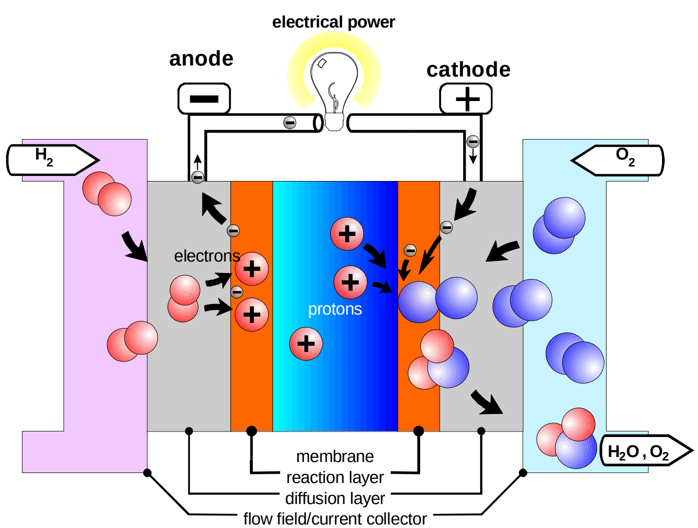
Field of application of porous electrodes

Batteries and supercaps

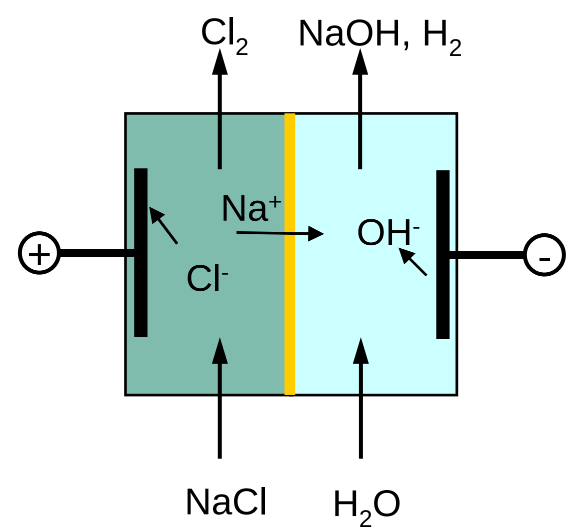
Water purification and treatment
(Bio)-Organic synthesis



Fuel Cells



Electrolysis (Water, NaCl, etc.)



Fuel cell overvoltage and current density / voltage characteristic

Hydrogen Oxidation Reaction (HOR):

$\eta_{H_2} = RT/2F\ i/i^*$

Oxygen Reduction Reaction (ORR):

$\eta_{O_2/air} = RT/[(1-\alpha)2F]\ [\ln i - \ln i^*]$

Ohmic loss

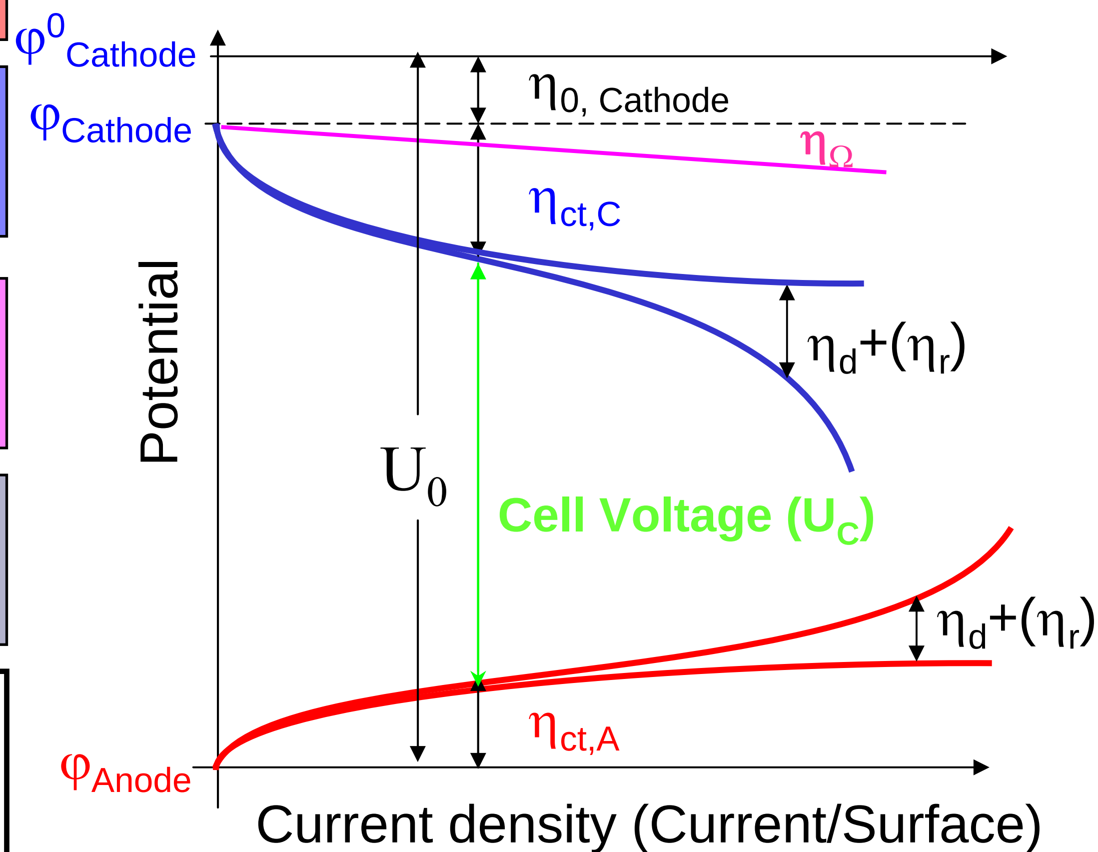
$\eta_\Omega = iR$

Transport limitation (diffusion)

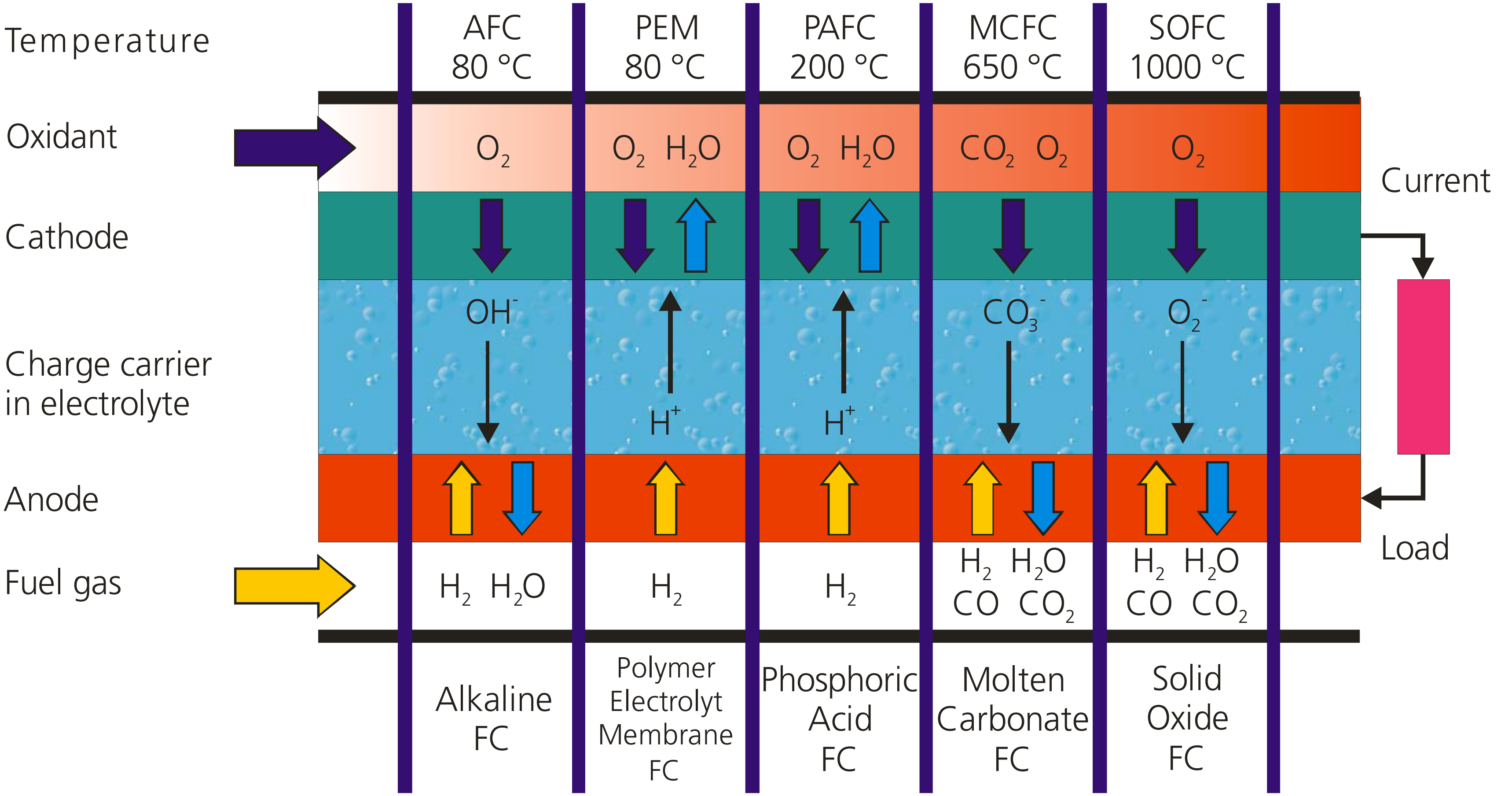
$\eta_d = -RT/2F \ln(1 - i/i_{lim})$

Fuel cell voltage

$U_C = U_0 - \eta_{ct,H_2} - \eta_{ct,O_2/air} - \eta_d - \eta_\Omega$



Schematic representation of main types of fuel cells



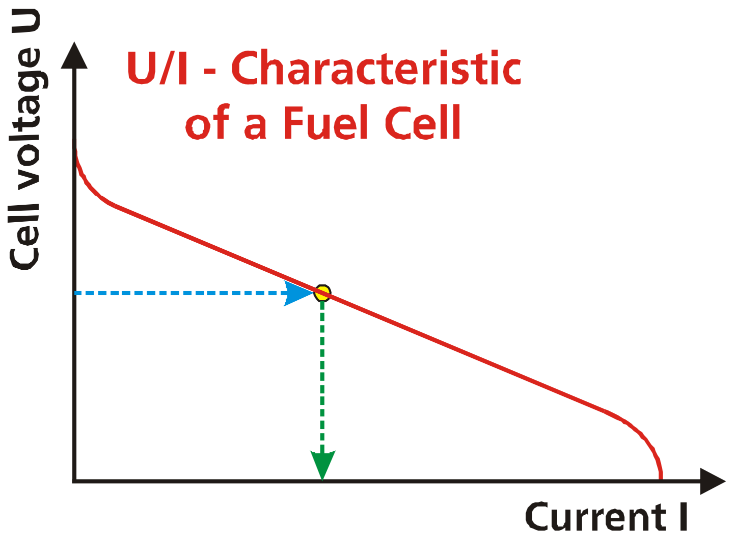
Measuring methods used for fuel cell and fuel cell components characterization : in-situ und ex-situ methods

- **In-situ measuring methods**
  - Current-voltage characteristic (U(i))
  - Electrochemical Impedance Spectroscopy (EIS)
    - Local and time resolved
  - Cyclic Voltammetry (CV)
  - Current interruption (CI))
  - Chronopotentiometry (CP) und Chronoamperometry (CA)
  - Current density distribution

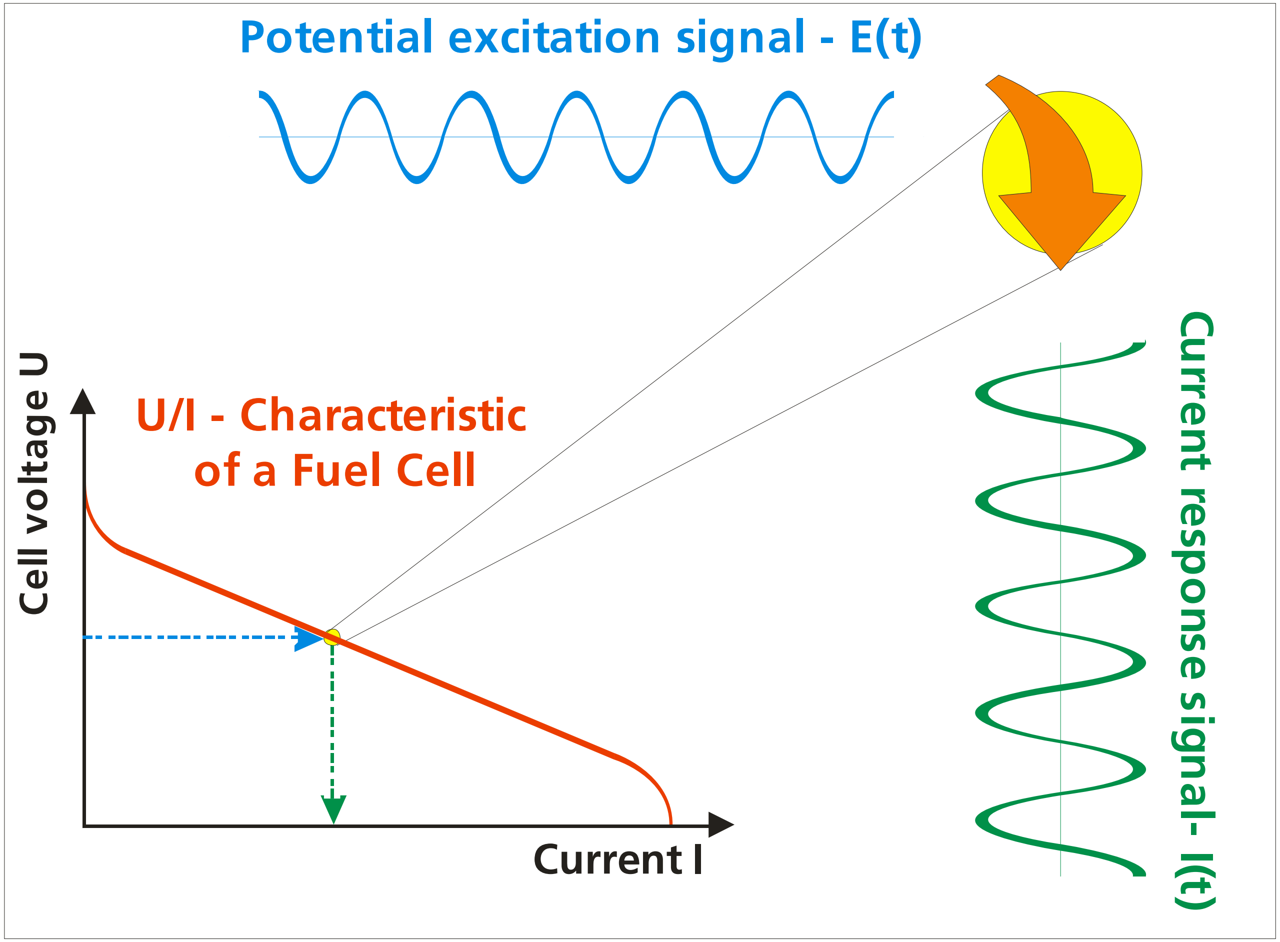
Ex-situ measuring methods used for fuel cell and fuel cell components characterization

- Scanning electron microscopy (SEM) and Transmission electron microscopy (TEM)
- Energy dispersive X-ray spectroscopy (EDS)
- X-ray photoelectron spectroscopy (XPS)
- X-Ray Diffraction (XRD)
- Thermal gravimetric analysis (TGA)
- Porosimetry (Hg-Porosimetry)
- Measurement of the specific surface area (BET-measurement)
- Determination of gas permeability

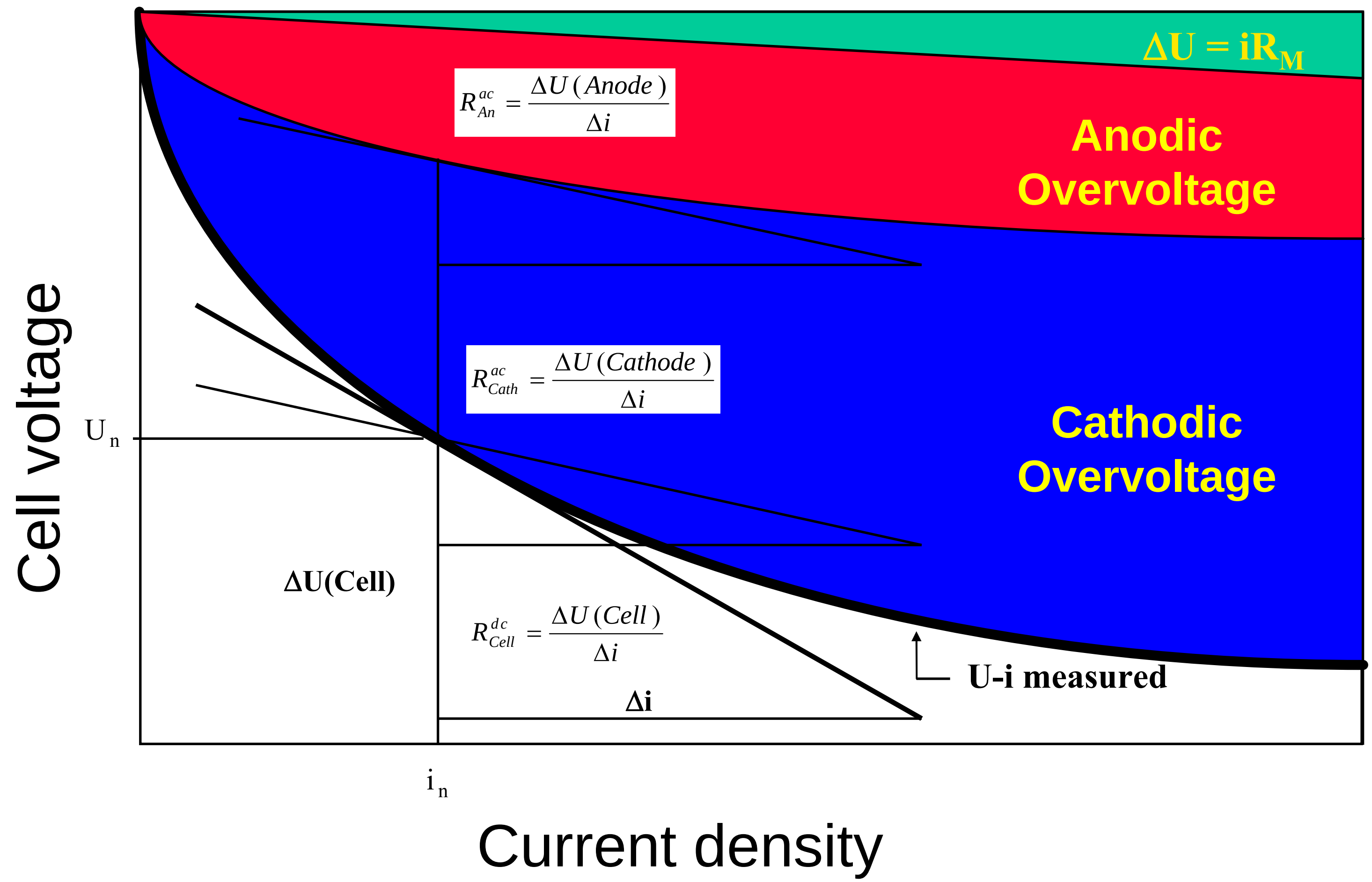
Electrochemical Impedance Spectroscopy: Application to Fuel Cells



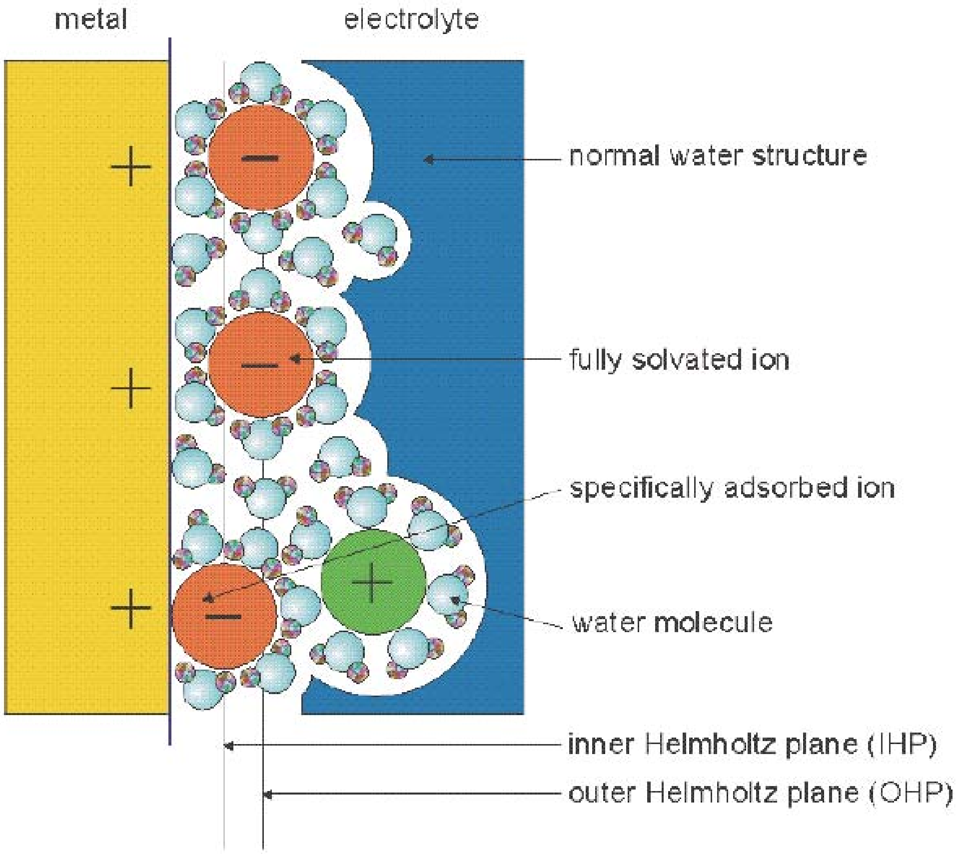
Electrochemical Impedance Spectroscopy: Application to Fuel Cells



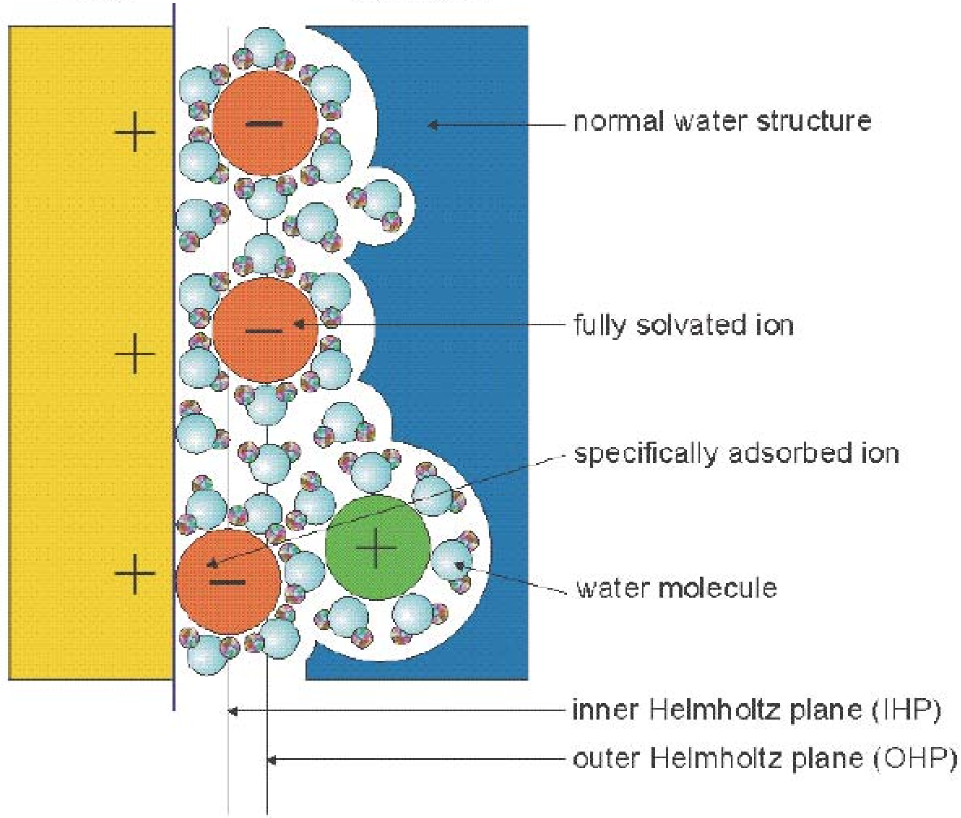
Schematic diagram of the U-i characteristic of PEFC and Electrochemical Impedance Measurements

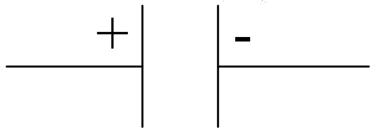


The Metal-Electrolyte Interface



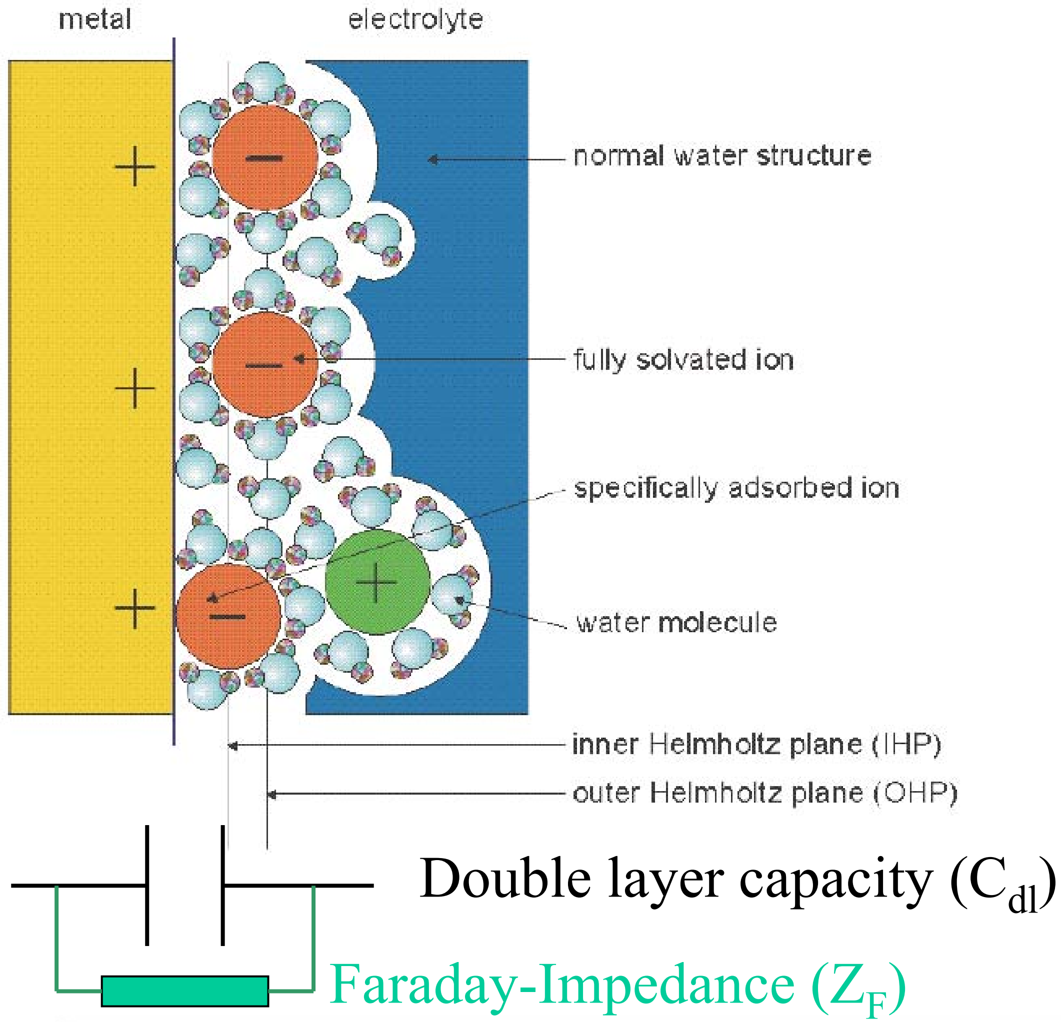
The Metal-Electrolyte Interface



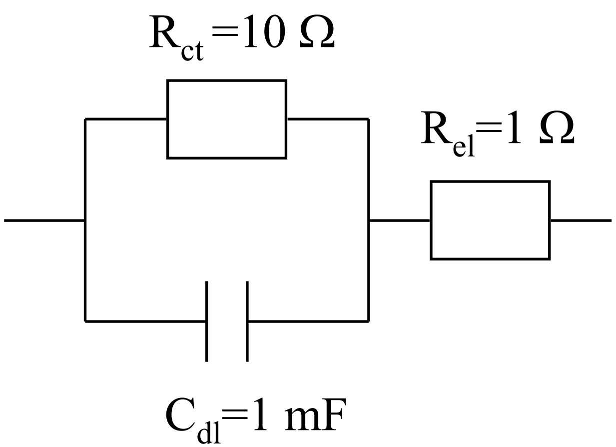


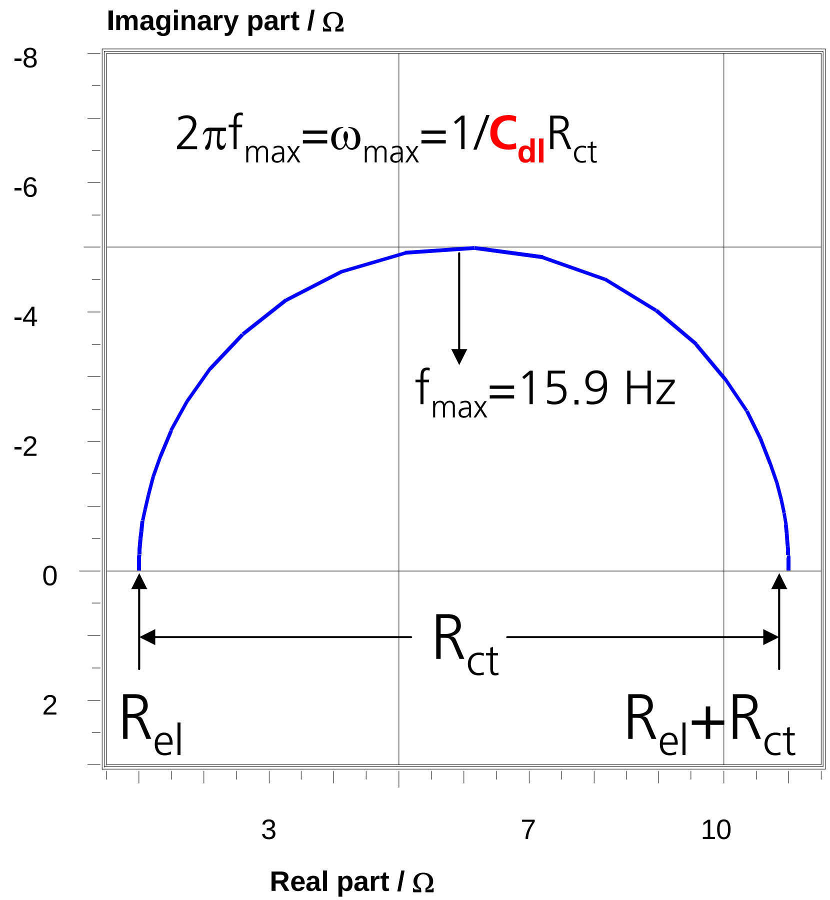
Double layer capacity (C_{dl})

The Metal-Electrolyte Interface

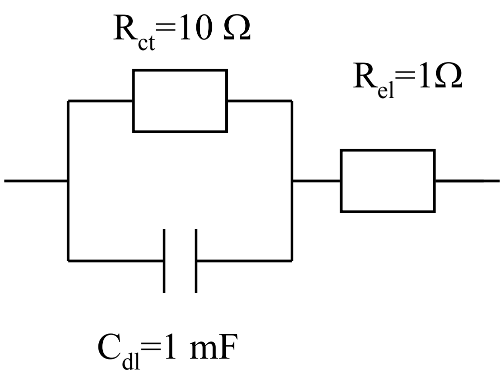


Impedance spectra of a simple electrochemical system ($Z_F = R_{ct}$): Nyquist representation



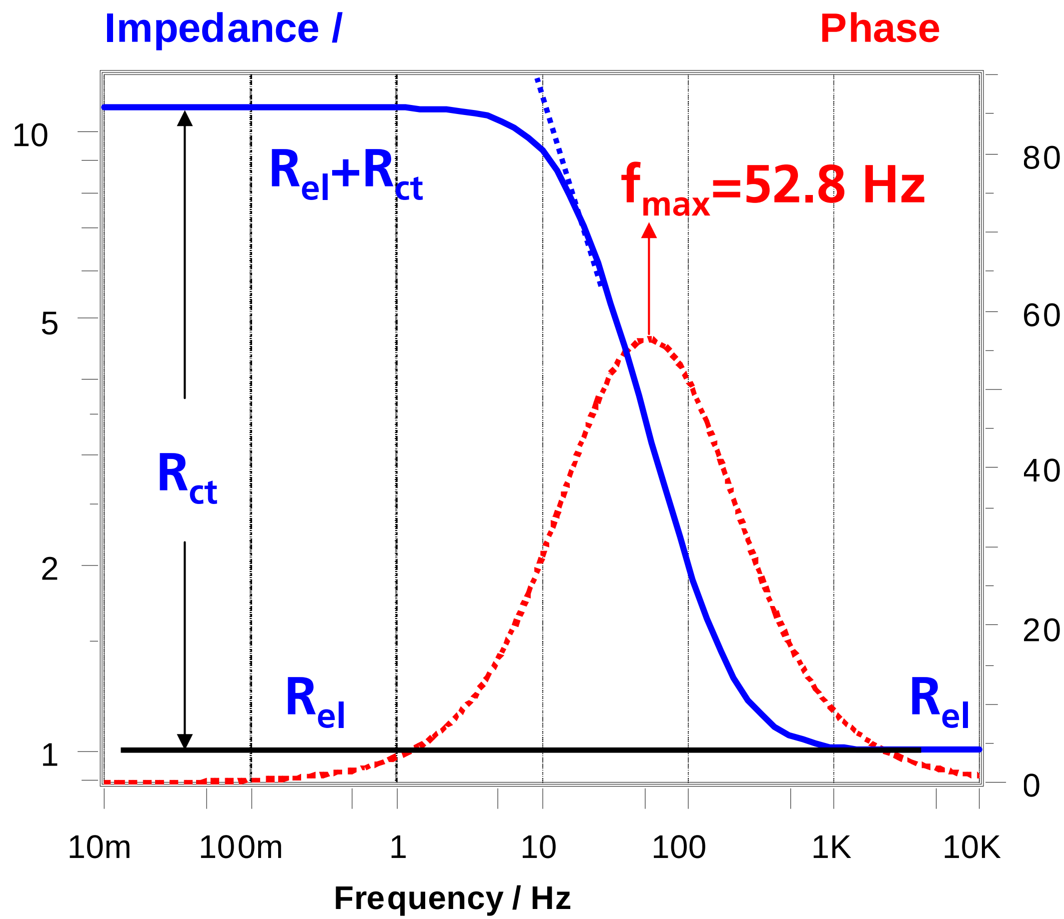


Impedance spectra of a simple electrochemical system ($Z_F=R_{ct}$): Bode representation



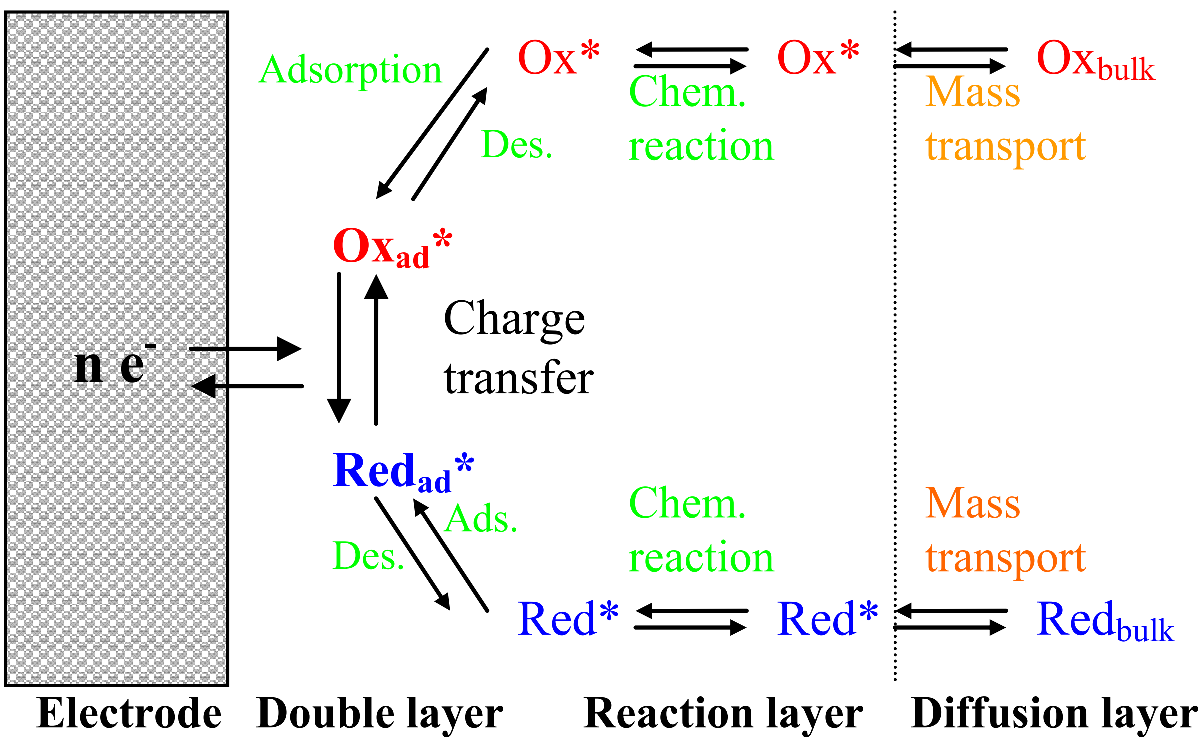
$2\pi f_{max}=(1/R_{ct}C_{dl})(1+R_{ct}/R_{el})^{1/2}$

at $\omega=2\pi f=1$: $Z_C=1/C_{dl}$ (------)

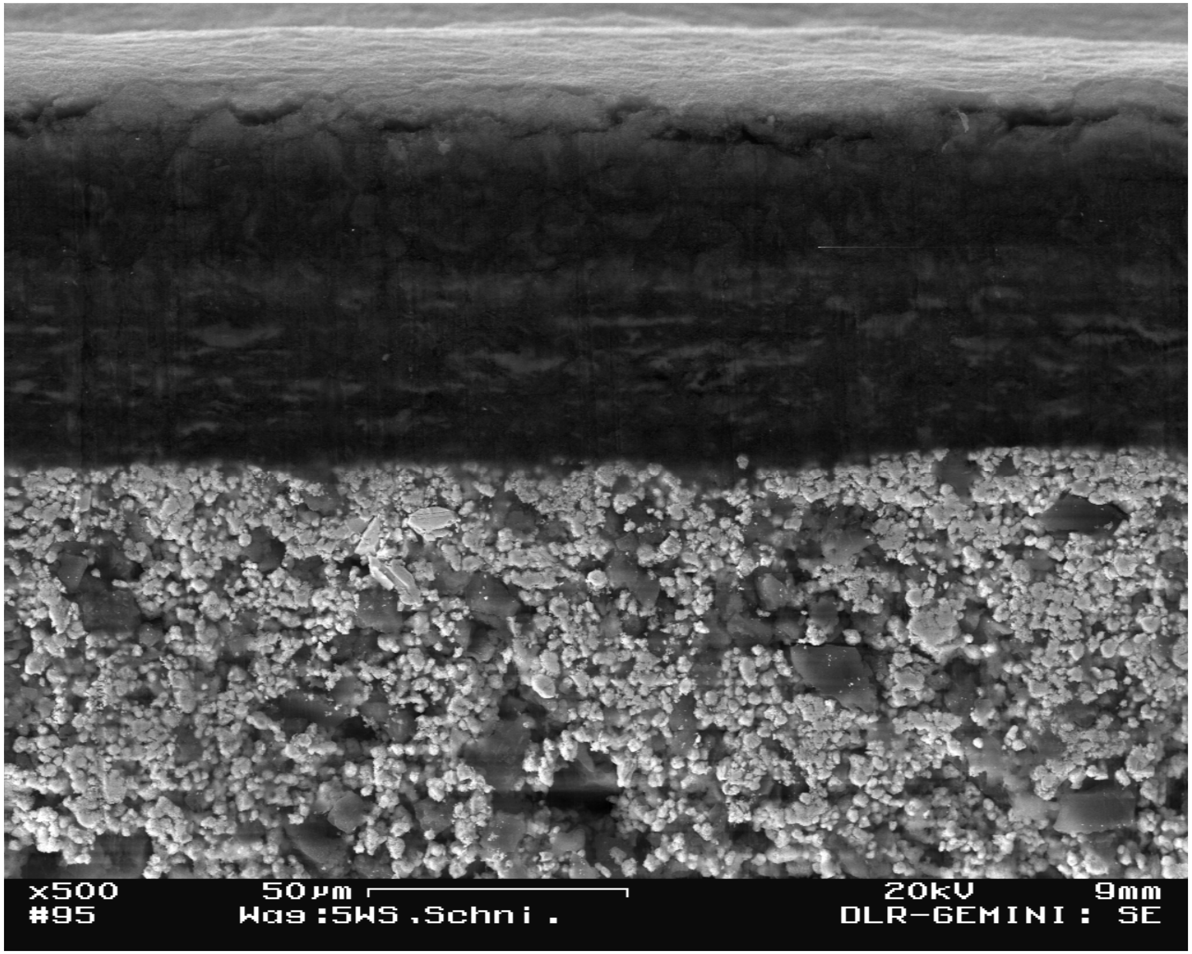


Schematic representation of different steps during electrochemical reaction as a function of distance from electrode surface

$$Ox + ne^- \leftrightarrow Red$$



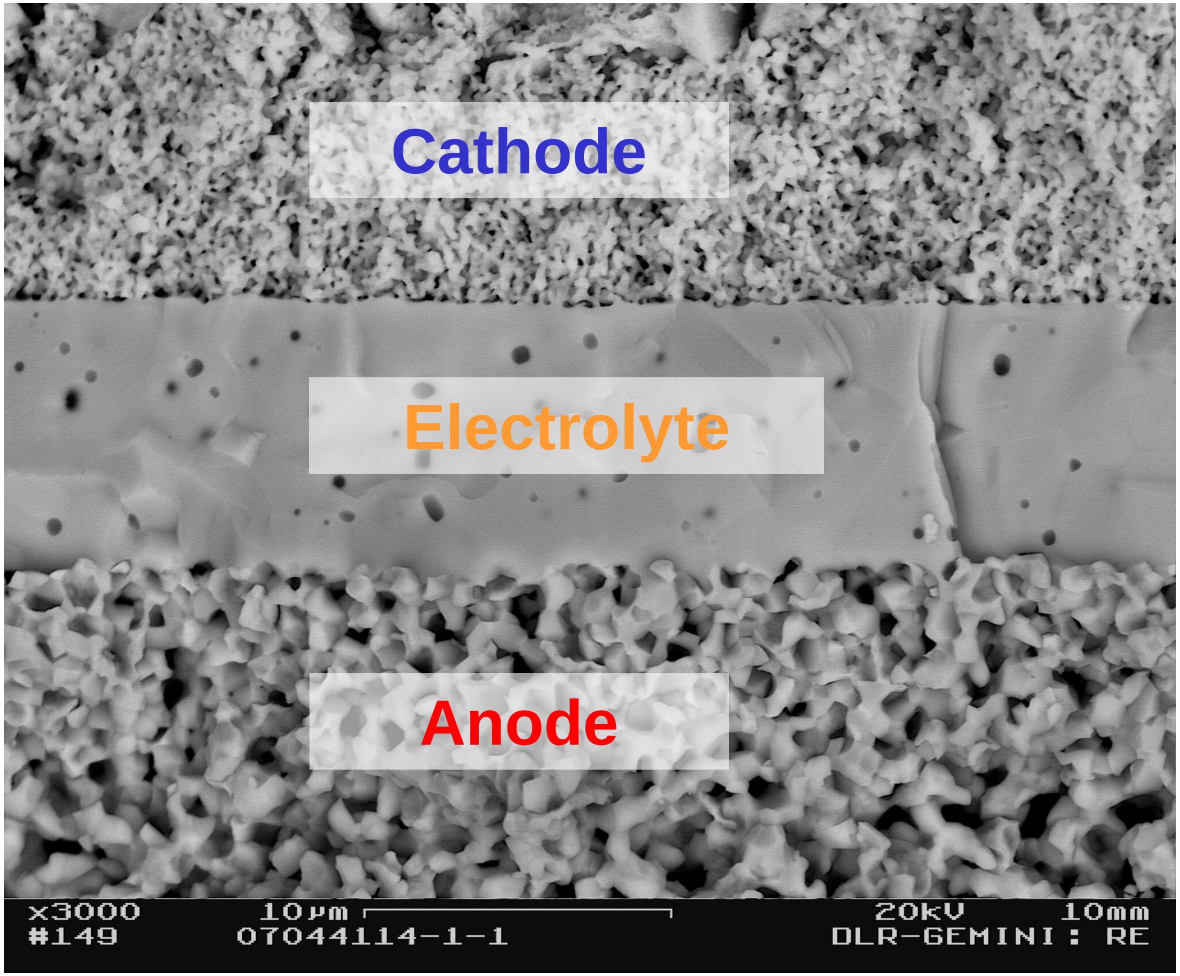
Multi-layer Gas Diffusion Electrodes with different porous layers



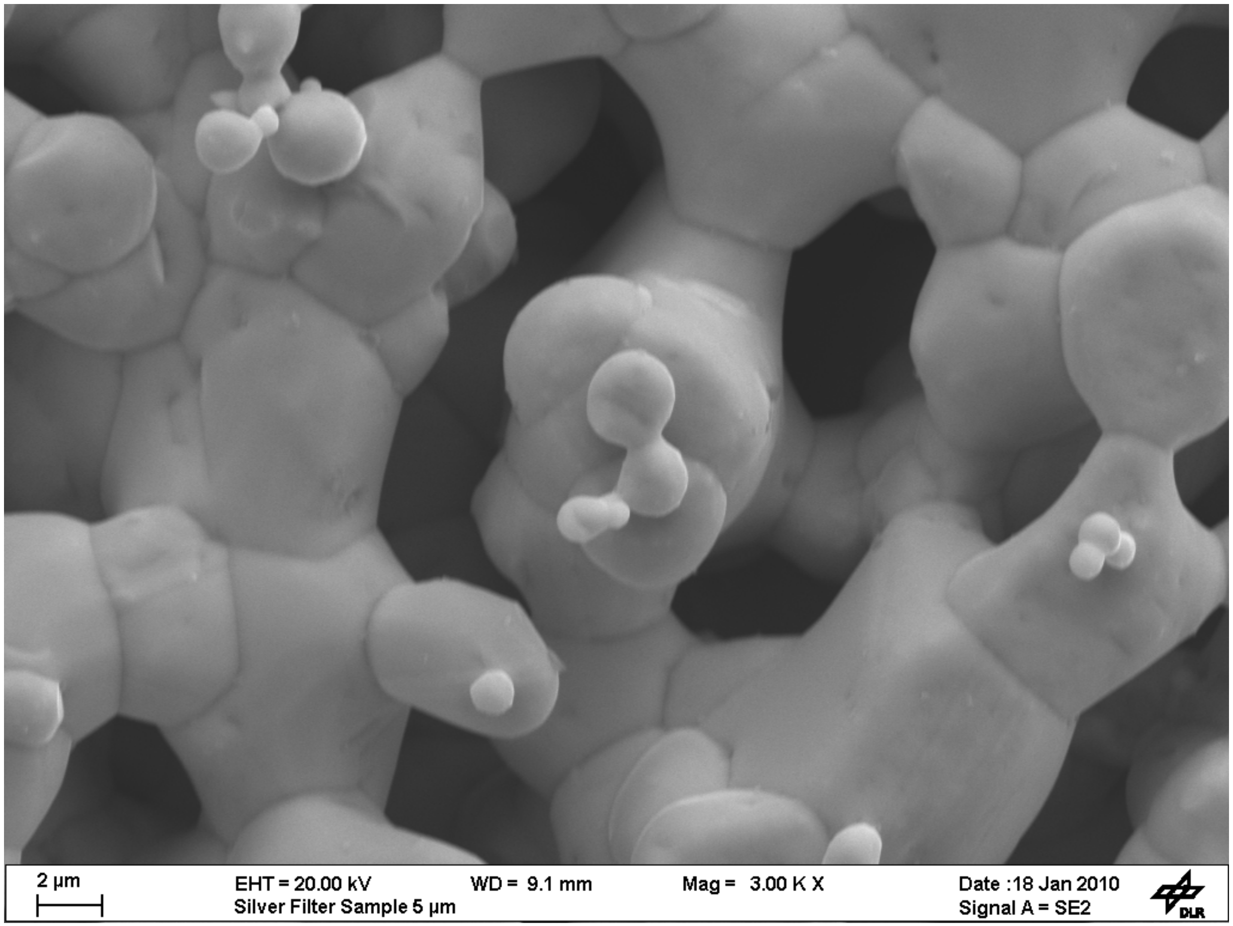
Carbon-PTFE Layer (Dry sprayed)

Ag-PTFE Layer (Rolled Layer)

SEM micrograph of a cross section of SOFC

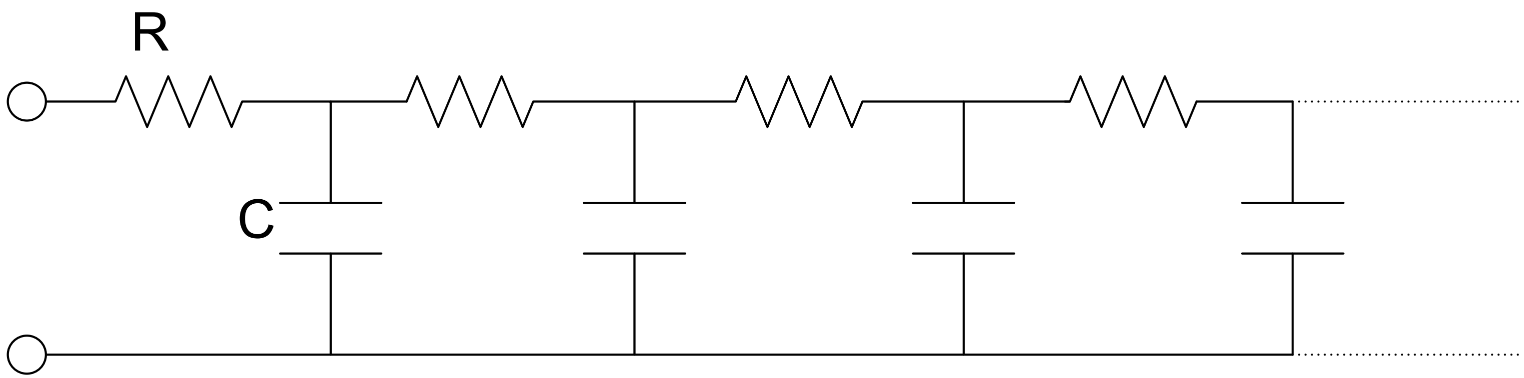


SEM micrograph of a porous silver membrane



Simple pore model of interface charging

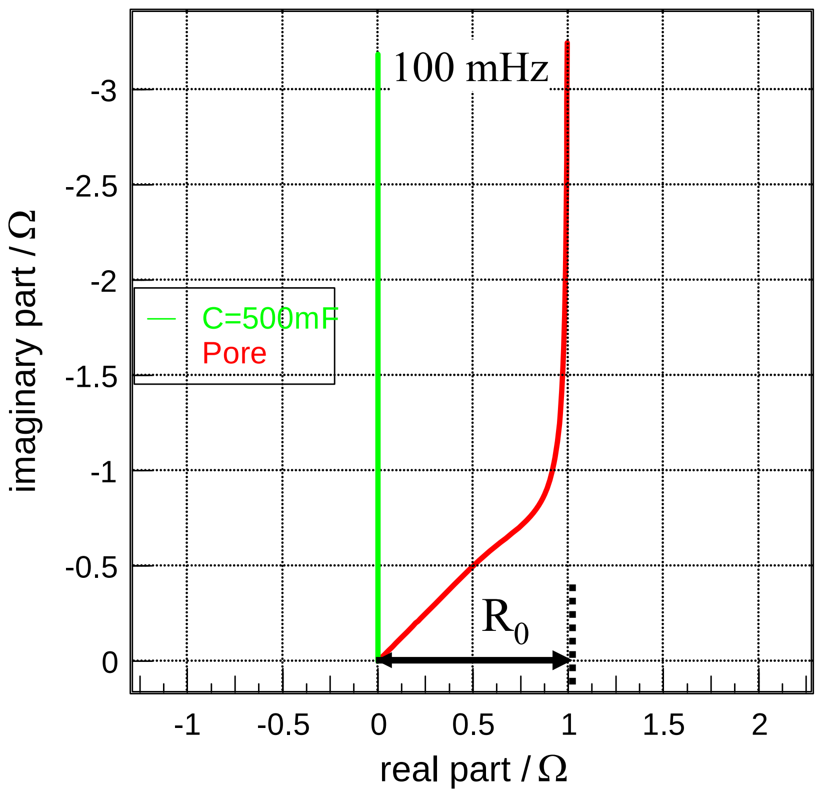
RC-transmission line of a flooded pore

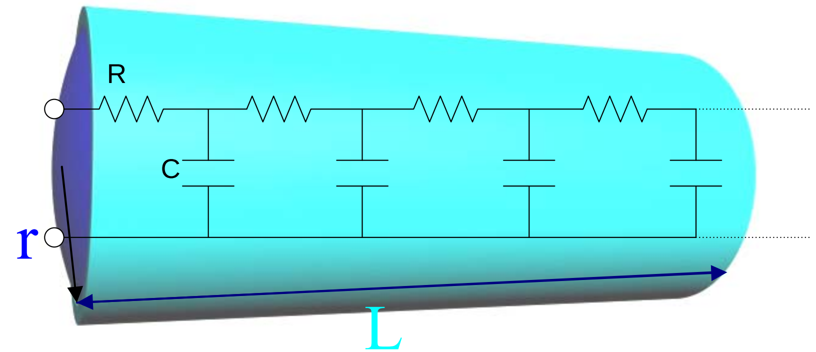


R = electrolyte resistance inside the pore per unit length
C = interface capacitance per unit length

$$Z(i\omega) = \sqrt{\frac{R}{i\omega C}} \coth \sqrt{i\omega RC}$$

Nyqusit representation of Impedance of RC-transmission line, model of a flooded pore





R = 3 Ω

C = 0.5 F

$$Z(i\omega) = \sqrt{\frac{R}{i\omega C}} \coth \sqrt{i\omega RC}$$

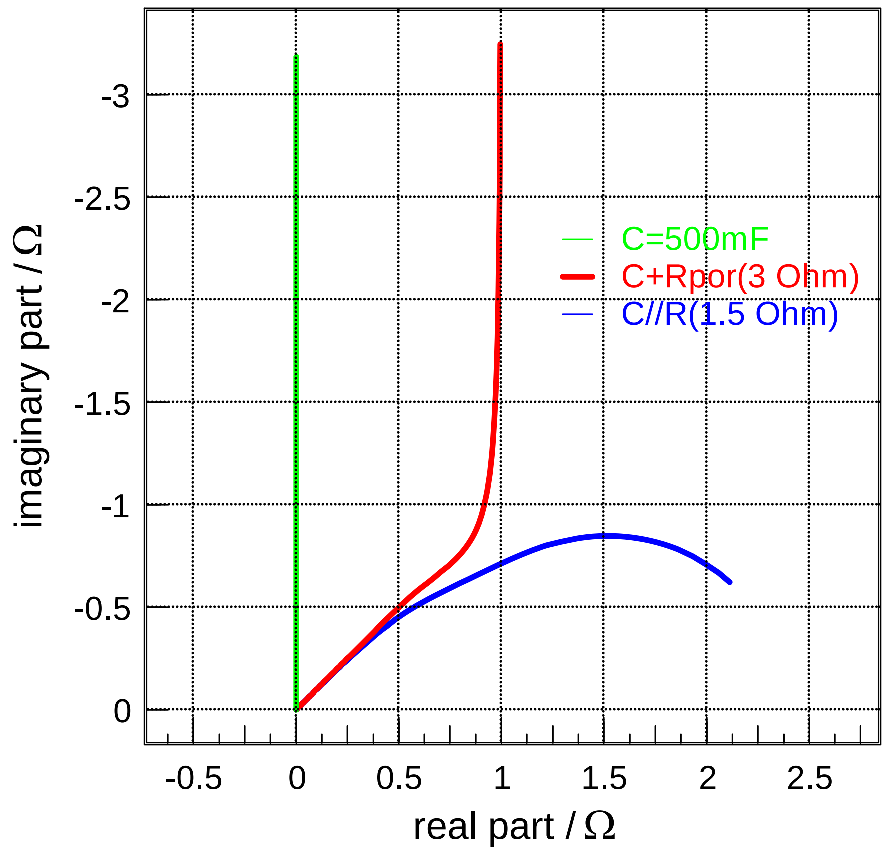
$$R_0 = R/3 = \delta L/3\pi r^2$$

δ = specific electrolyte resistance

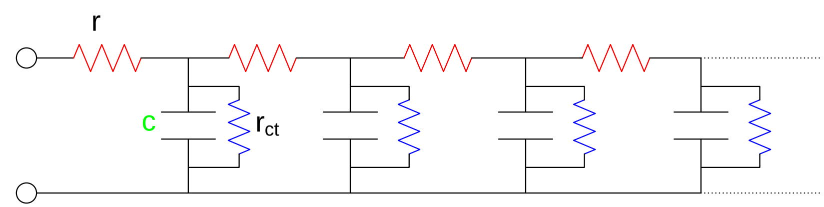
r = pore radius

L = pore lenght

Nyqusit representation of porous electrode impedance with faradaic impedance element



Simple pore model with faradaic processes in pores
RC-transmission line of a flooded pore

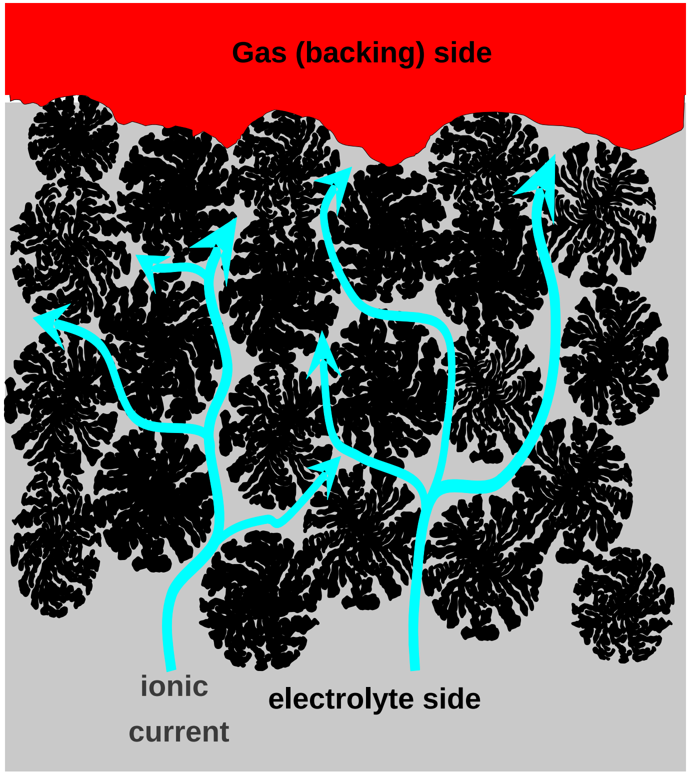


$r = 3\ \Omega$

$c = 500\ mF$

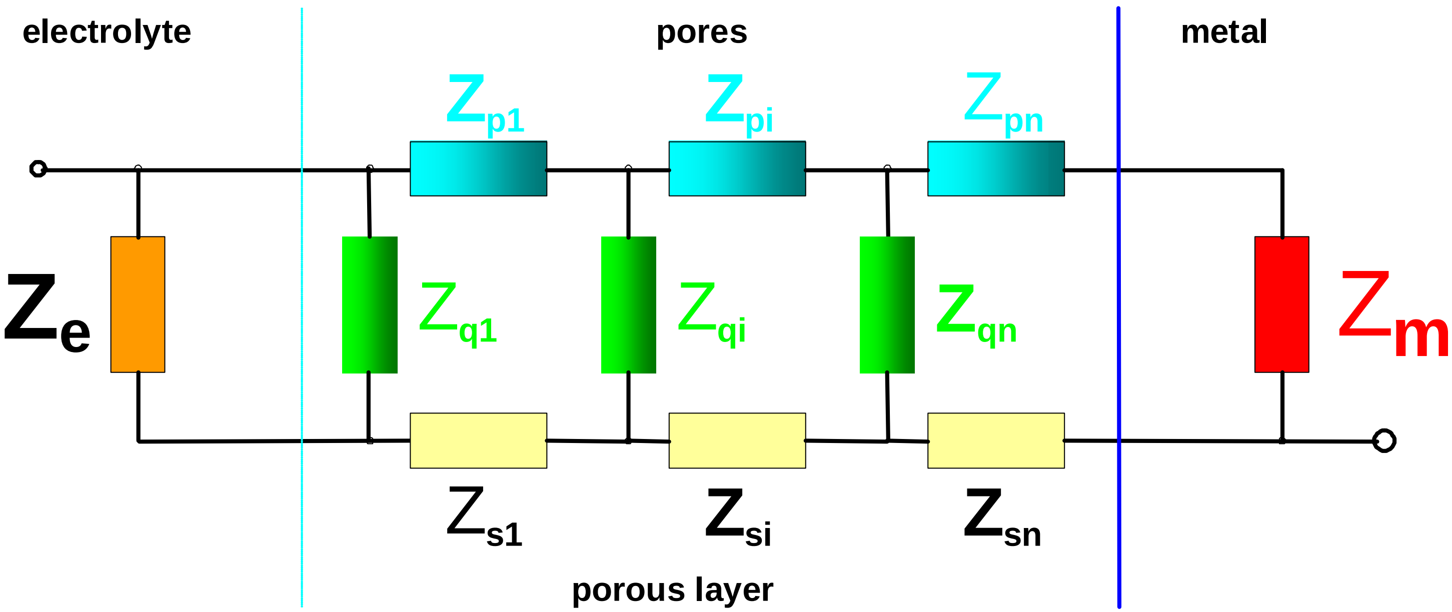
$r_{ct} = 1.5\ \Omega$

Theory of Agglomerated Electrodes



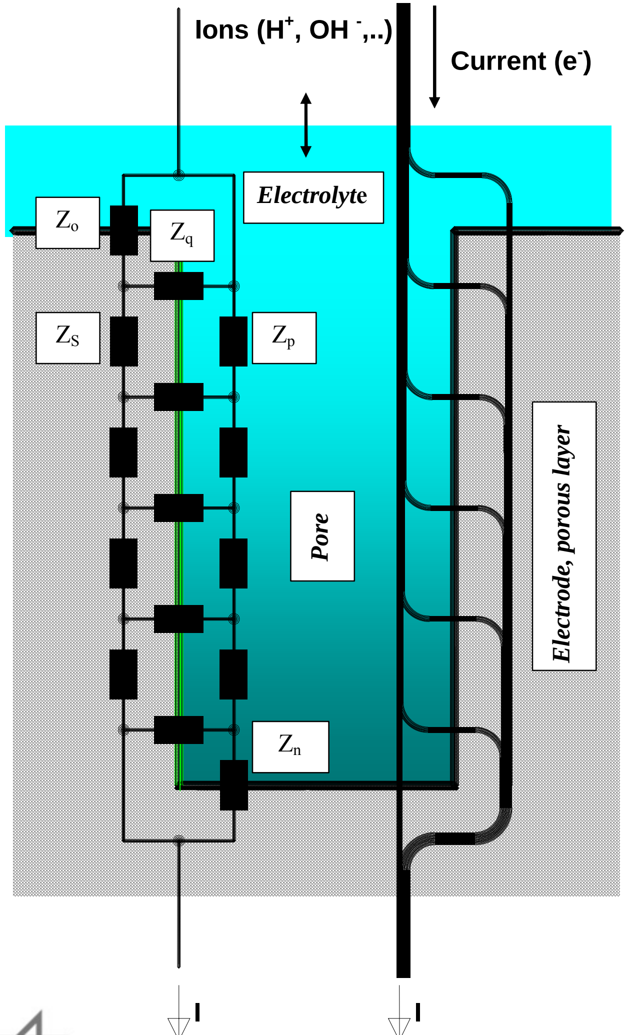
M. Eikerling, A.A. Kornyshev, E. Lust, *J. Electrochem. Soc.*, **152** (2005) E24

Cylindrical homogeneous porous electrode model (H. Göhr) I



H. Göhr in *Electrochemical Applications/97*, www.zahner.de

Cylindrical homogeneous porous electrode model (H. Göhr) II



$$Z^* = \sqrt{(Z_p + Z_s) \cdot Z_q}$$

$$Z^\# = \frac{Z_p \cdot Z_s}{(Z_p + Z_s)}$$

$$C = \cosh\left(\frac{Z_p + Z_s}{Z^*}\right)$$

$$S = \sinh\left(\frac{Z_p + Z_s}{Z^*}\right)$$

$$P = \frac{Z_p}{Z_p + Z_s}$$

$$q_0 = \frac{Z^*}{Z_o}$$

$$v = \frac{Z_p + Z_s}{Z^*}$$

$$q_n = \frac{Z^*}{Z_n}$$

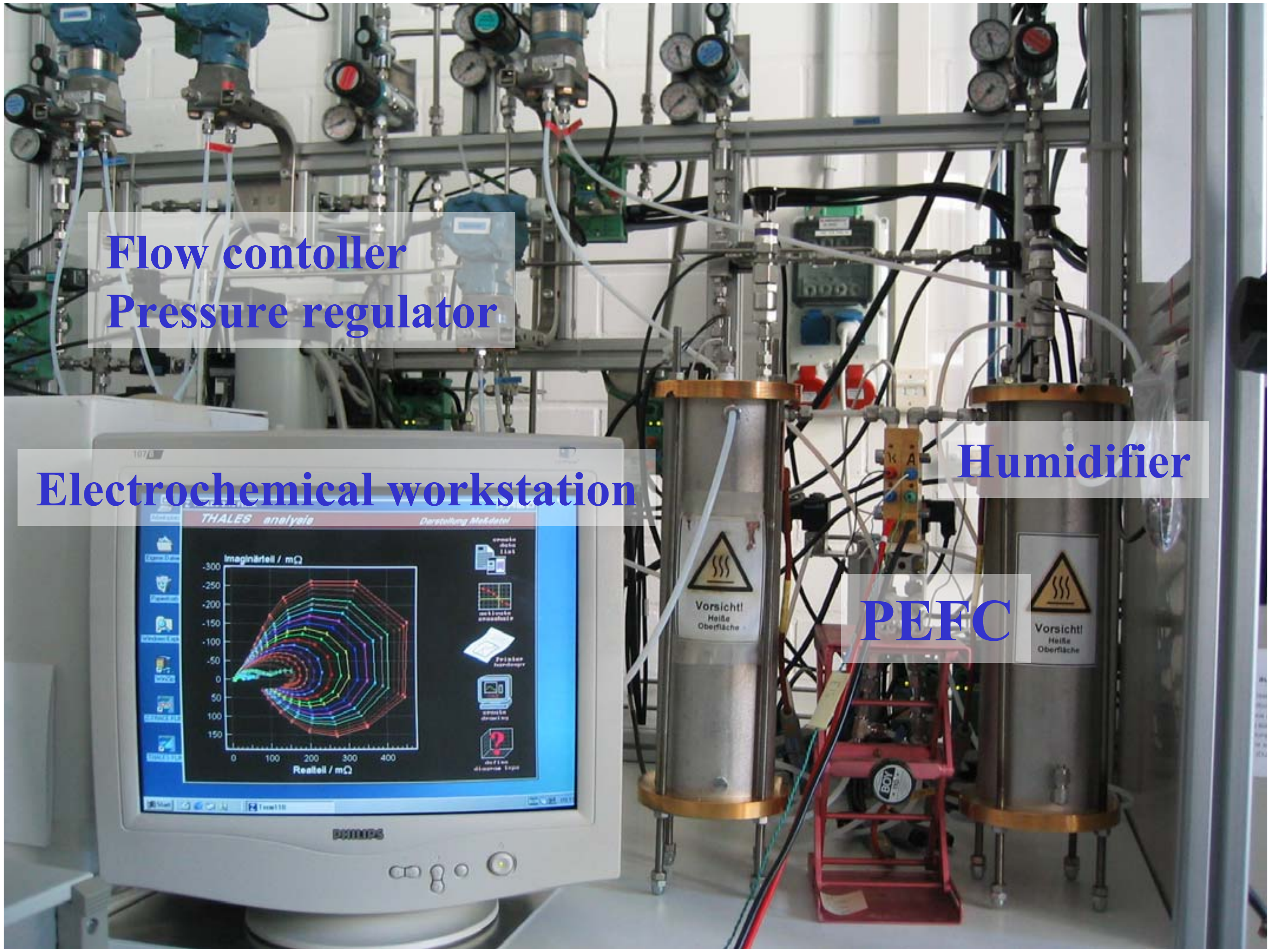
$$s = \frac{Z_s}{Z_p + Z_s} = 1\text{-}p$$

$$Z = Z^\# + Z^* \cdot \frac{C + (1 - C) \cdot 2 \cdot p \cdot s + S \cdot (p^2 \cdot q_n + s^2 \cdot q_o)}{S \cdot (1 + q_n \cdot q_o) + C \cdot (q_n + q_o)}$$

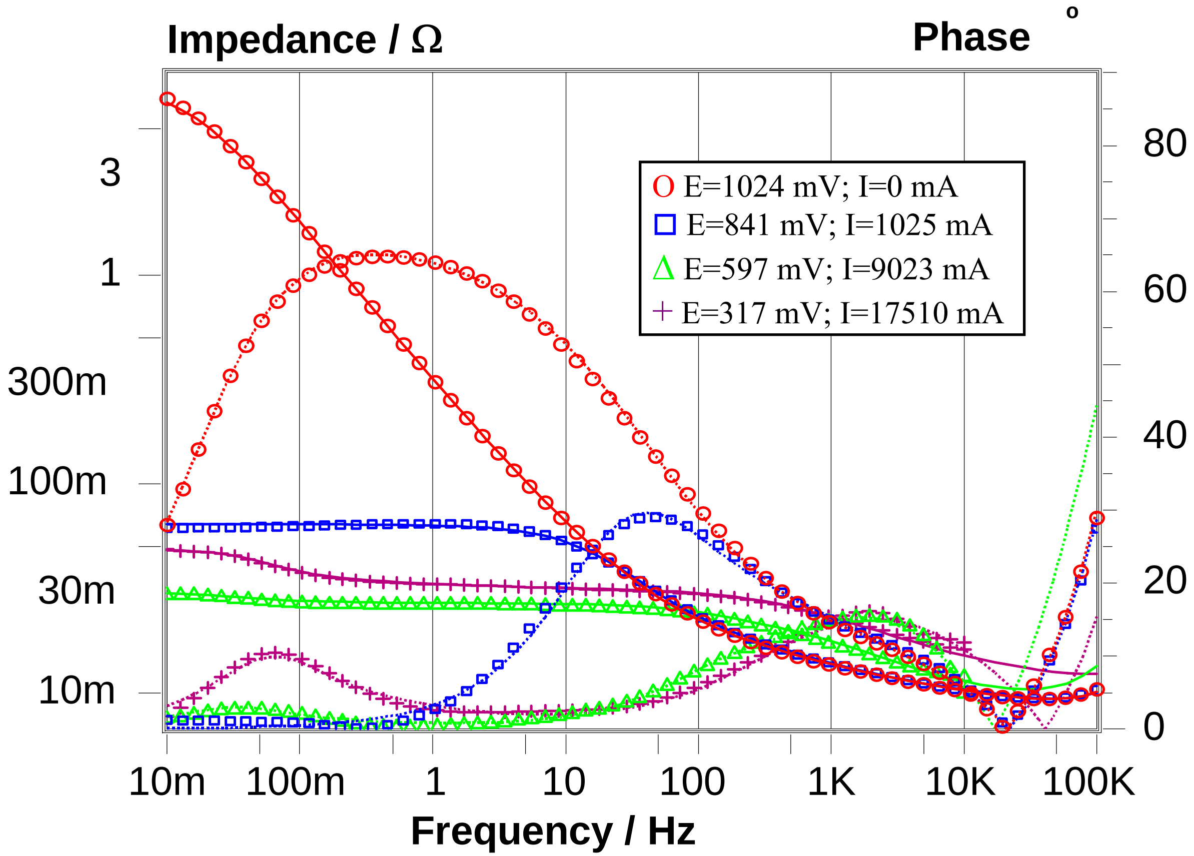
Brief Overview of Porous electrode models and Applications

Authors	Reference	Model and system
J. -P Candy, P Fouilloux, M. Keddam, H. Takenouti	Electrochim. Acta, 26(1981) 1029	Ni in alkaline solution
R. De Levie	Electrochim. Acta, 8(1963) 751	Transmission line model,
J.S. Newman and C.W. Tobias	J. Electrochem. Soc., 109(1962) 1183	Steady-state
J. Giner, C. Hunter	J. Electrochem. Soc., 116(1969) 1124	Flooded-agglomerate model, Pt-GDE, OCR in alkaline solution
K. Mund, F.v. Sturm	Electrochim. Acta, 20(1975) 463	HOR on Ni in alkaline solution
S. Sunde,	Electrochim. Acta, 42(1997) 2637	Composites, SOFC
P. Björnbom	Electrochim. Acta, 32(1987) 115	Steady state model
R. Holze, W. Vielstich	J. Electrochem. Soc., 131(1984) 2298	OCR in alkaline solution
T.E. Springer, I.D. Raistrick	J. Electrochem. Soc., 136(1989) 1594	Flooded-agglomerate and thin film model, differential element of a pore wall
H. Göhr	Poster ISE Erlangen, 1983	Homogeneous porous model, Pb in sulfphuric acid
G. Paasch, K. Micka, P. Gersdorf	Electrochim. Acta, 38(1993) 2653	Macrohomogeneous porous electrode model
W. Scheider	J. Phys. Chem., 79(1975) 127	Model with pore branching
S. Srinivasan, H. D. Hurwitz, J. O'M Bockris	J. Chem. Phys., 46(1967) 3108	Thin film model
M. Kramer, M. Tomkiewicz	J. Electrochem. Soc. 131(1984)	Stochastic approach with interpenetrating network
A. Winsel, E. Bashtavelova	J. Power Sources, 73(1998) 242	Agglomerate-of-spheres model
M. Tomkiewicz, B. Aurian-Blajeni	J. Electrochem. Soc. 135(1988) 2743	True effective medium approach
H. Keiser, K.D. Beccu, M.A. Gutjahr	Electrochim. Acta, 21(1976) 539	Various geometries of single pore, Ni-GDE

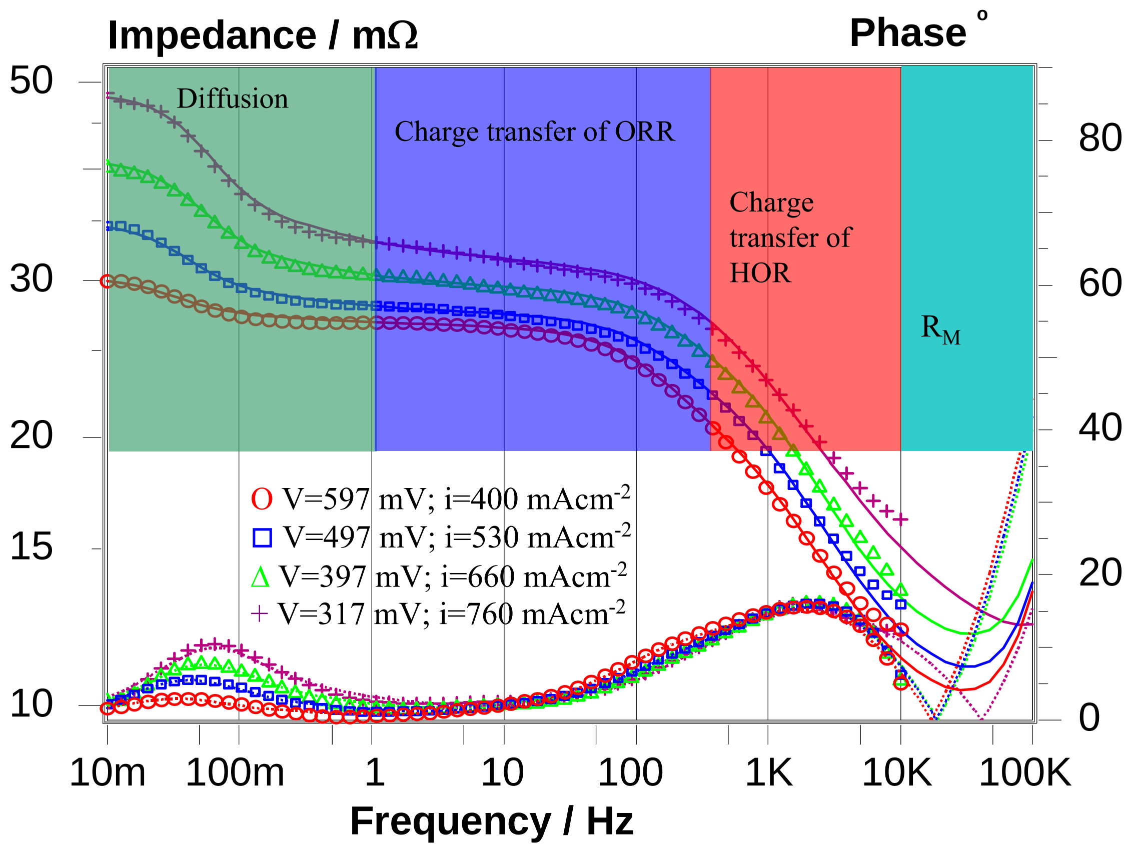
Electrochemical Impedance Spectroscopy: Experimental Set-up



Bode diagram of measured EIS at different cell voltages (current densities) I

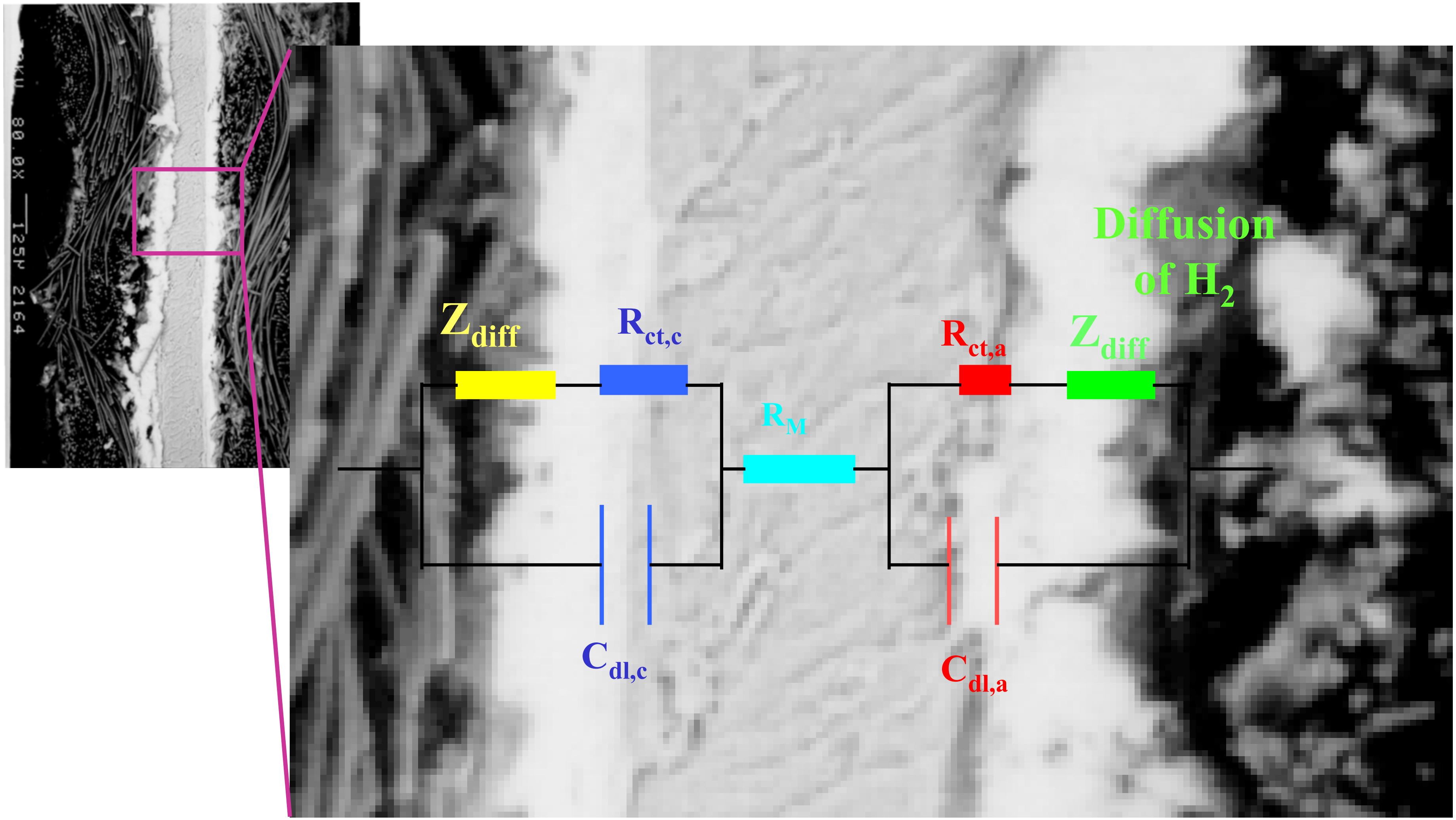


Bode diagram of measured EIS at different cell voltages (current densities) II



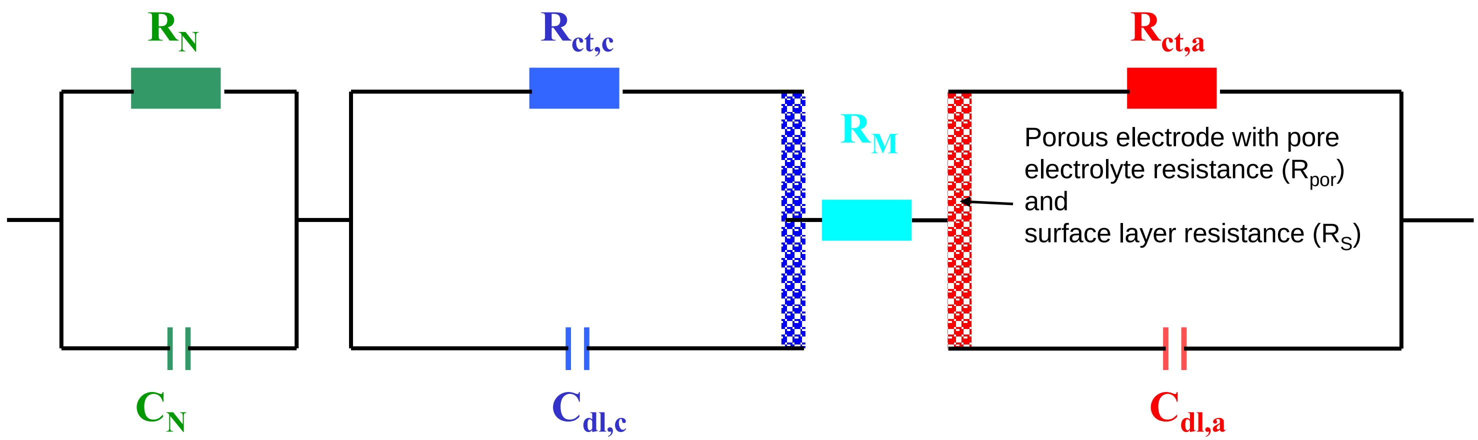
N. Wagner, K.A. Friedrich, *Dynamic Operational Conditions*. In: J. Garche, C. Dyer, P. Moseley, Z. Ogumi, D. Rand and B. Scrosati, editors. Encyclopedia of Electrochemical Power Sources, Vol. 2. Amsterdam: Elsevier, 2009, pp. 912-930

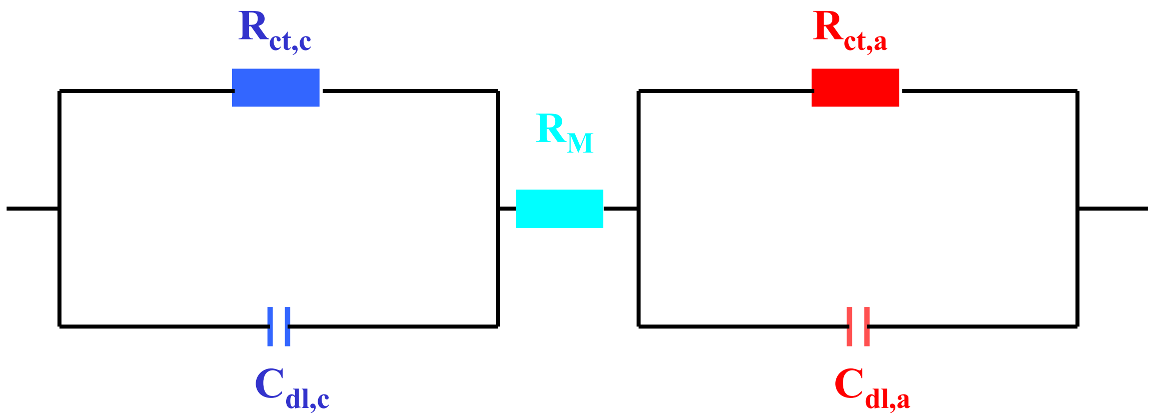
Common Equivalent Circuit for Fuel Cells



EIS at Polymer Fuel Cells (PEFC):

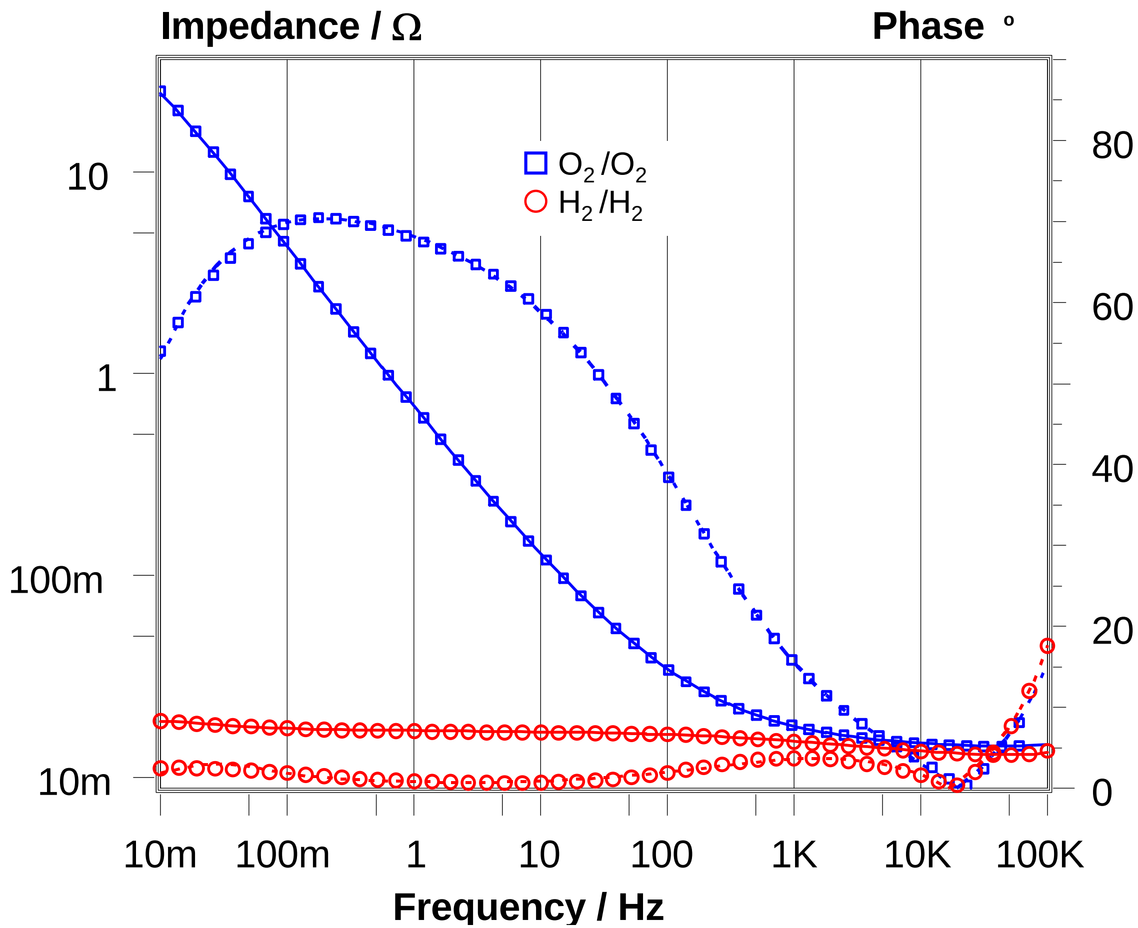
Common equivalent circuit and boundary case





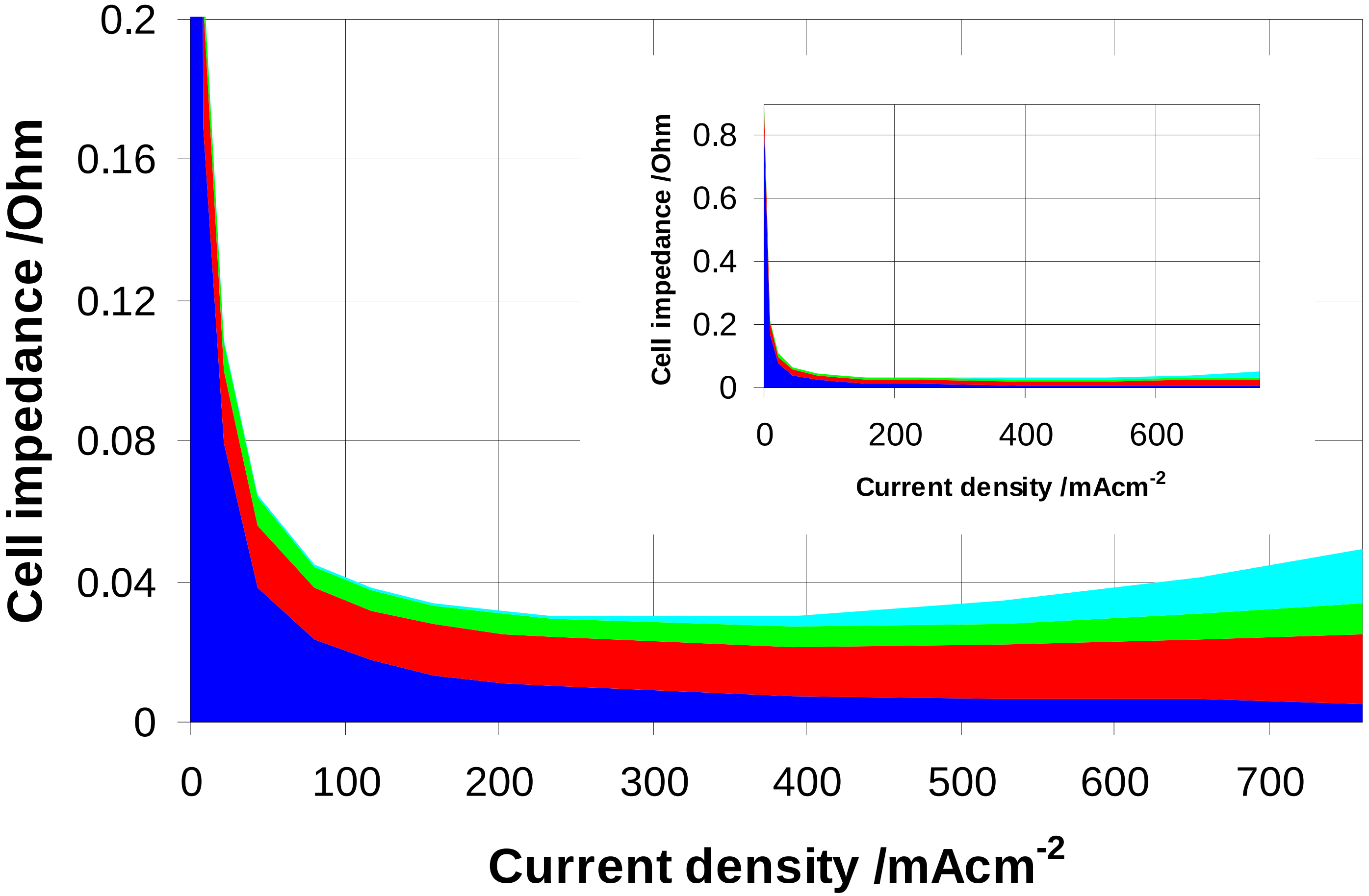
Equivalent circuit of the PEFC: anode and cathode simulated without pores, without diffusion (valid for example at lower current densities)

Bode diagramm of the EIS, measured at the PEFC at 80°C, symmetrical gas supply of the cell



EIS at Polymer Fuel Cells (PEFC):

Contributions to the cell impedance at different current densities



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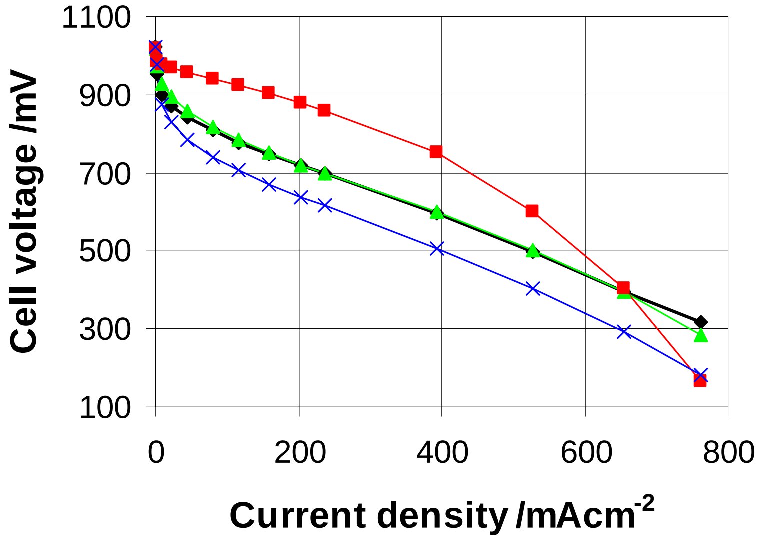
Evaluation of the U-i characteristics from EIS



- ◆ measured curve: $U_n = f(i_n)$
- ■ calculated curve: $U_n = i_n R_n$ (without integration)
- Δ calculated curve using method II: $U_n = a_n i^2_n + b_n i_n + c_n$
- x calculated curve using method I: $U_n = a_n i_n + b_n$

$$R_n = \frac{\partial U}{\partial I}\Big|_n$$

Integration method I:

$$U_n = U_{n-1} - \tfrac{1}{2}\left(\frac{\partial U}{\partial I}\Big|_{n-1} + \frac{\partial U}{\partial I}\Big|_n\right) * (I_n - I_{n-1})$$

Integration method II:

$$U_n = a_n I_n^2 + b_n I_n + c_n \quad \text{with:}$$

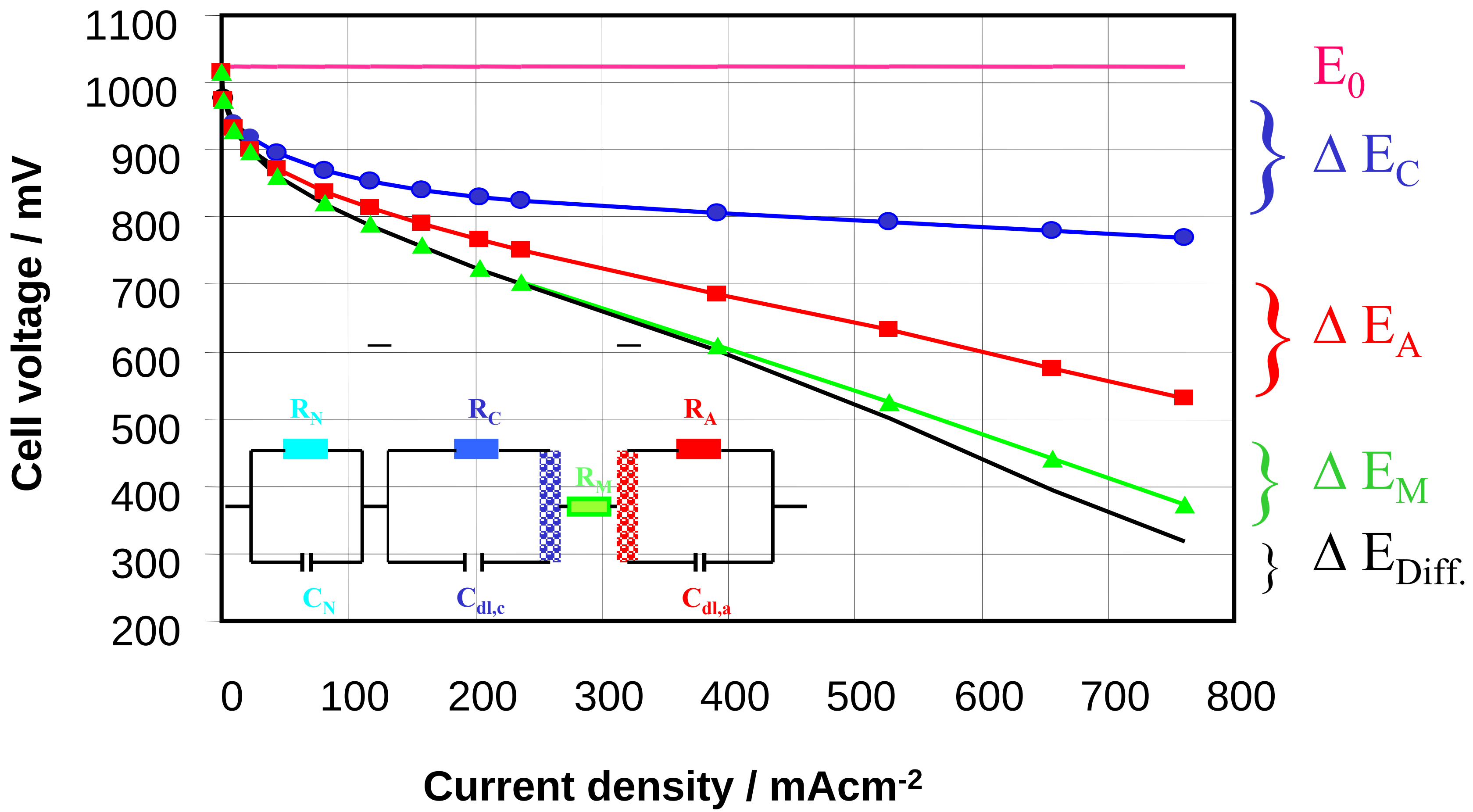
$$a_n = \frac{R_{n+1} - R_n}{2(I_{n+1} - I_n)}$$

$$b_n = R_{n+1} - 2 a_n I_{n+1}$$

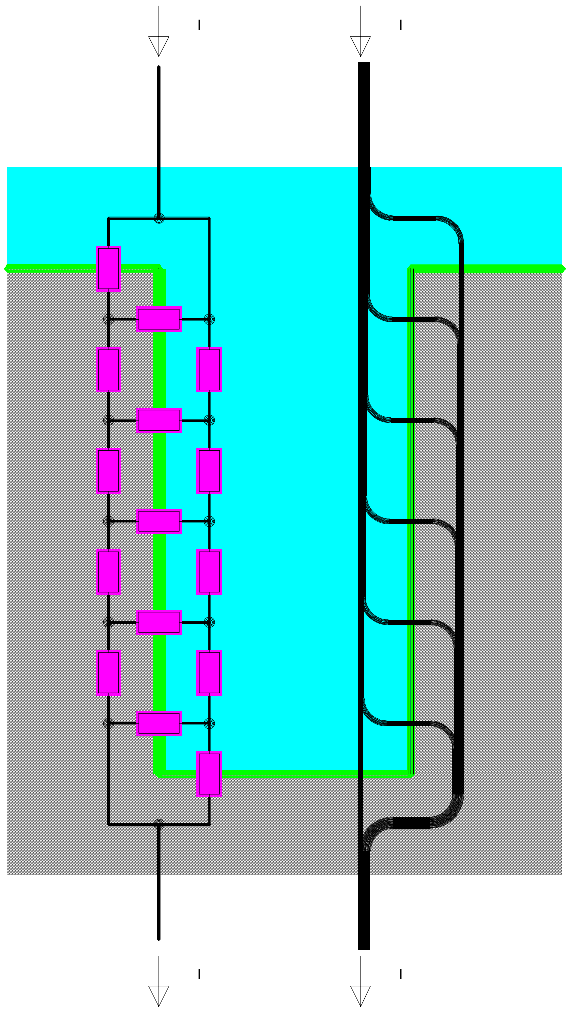
$$c_n = U_{n-1} - a_n I_{n-1}^2 - b_n I_{n-1}$$

EIS at Polymer Fuel Cells (PEFC):

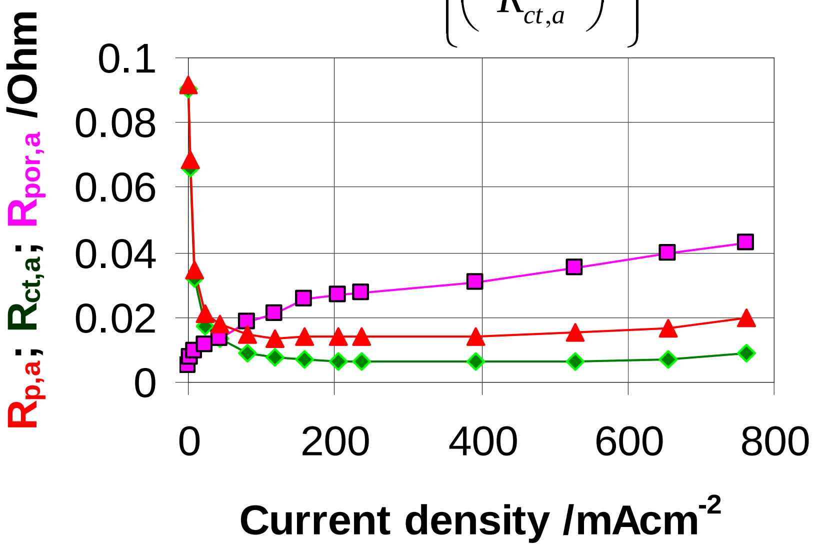
Contributions to the overal U-i characteristic determined by EIS



Evaluation of EIS with the porous electrode model



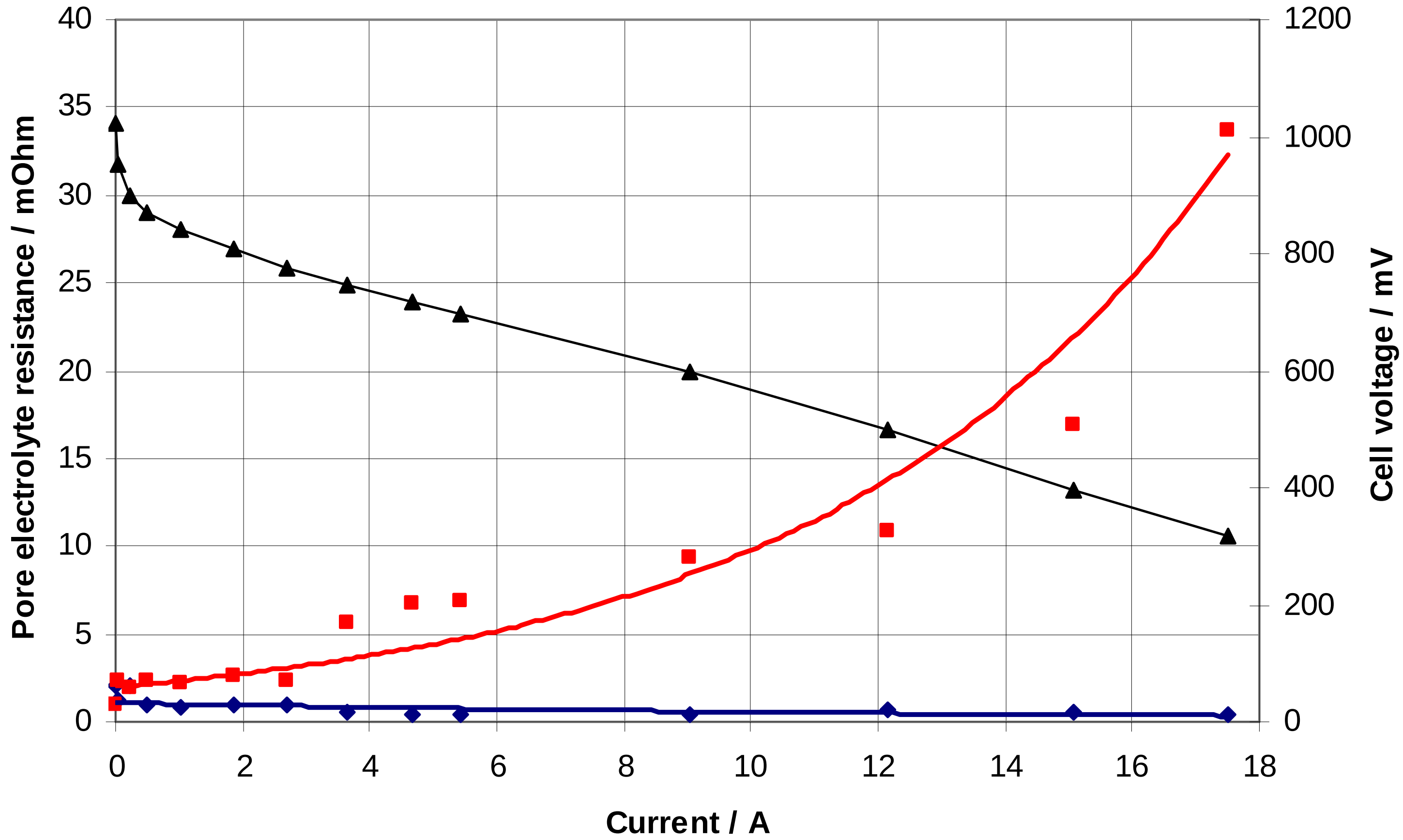
$$R_{p,a} = \frac{(R_{por,a} \cdot R_{ct,a})^{\frac{1}{2}}}{\tanh\left\{\left(\frac{R_{por,a}}{R_{ct,a}}\right)^{\frac{1}{2}}\right\}}$$



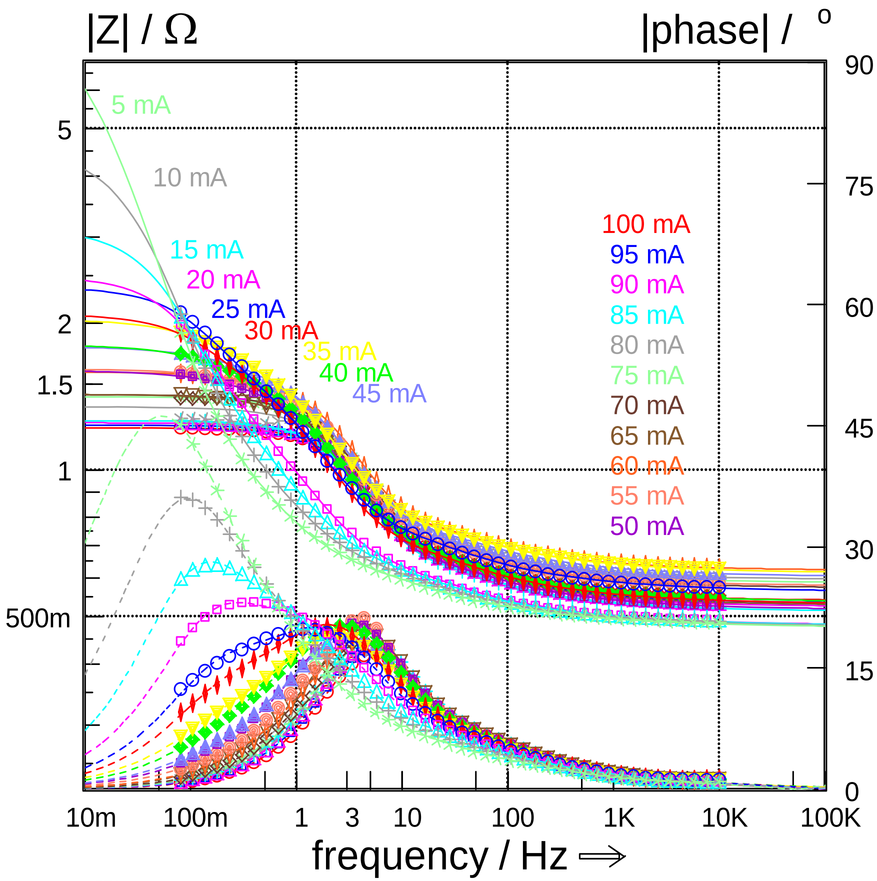
Porous electrode resistance ($R_{p,\ a}$), charge transfer resistance ($R_{ct,\ a}$) and electrolyte resistance ($R_{por,\ a}$) in the pore of the anode at different current densities

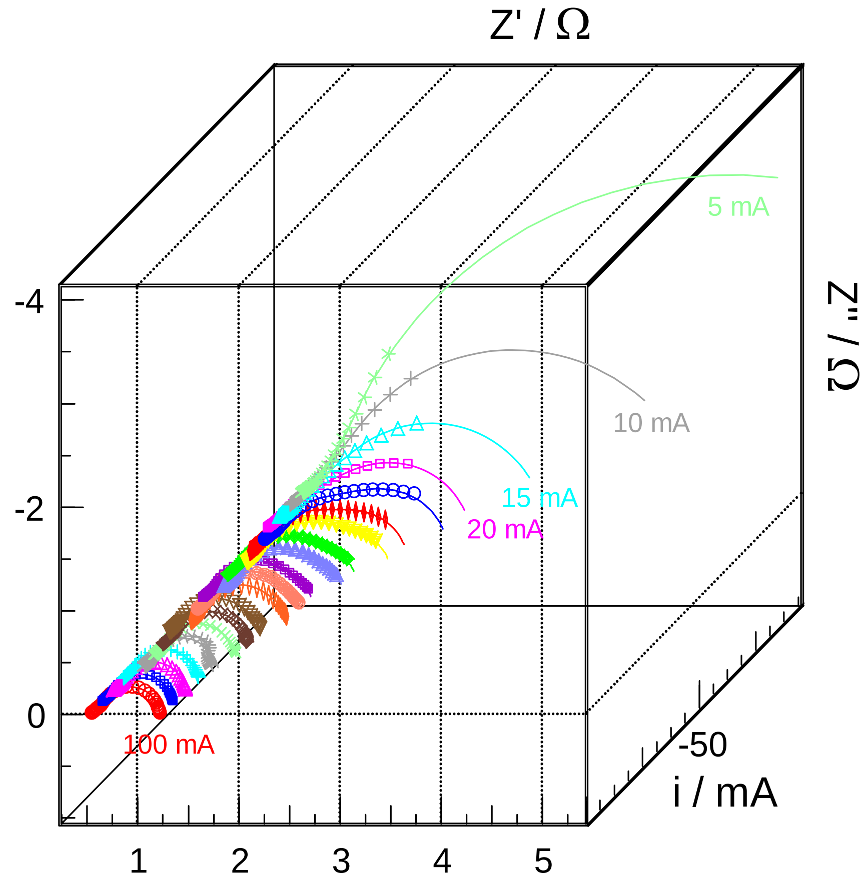
Evaluation of EIS with the porous electrode model

i-V characteristic and current dependency of pore electrolyte resistance of the anode and cathode

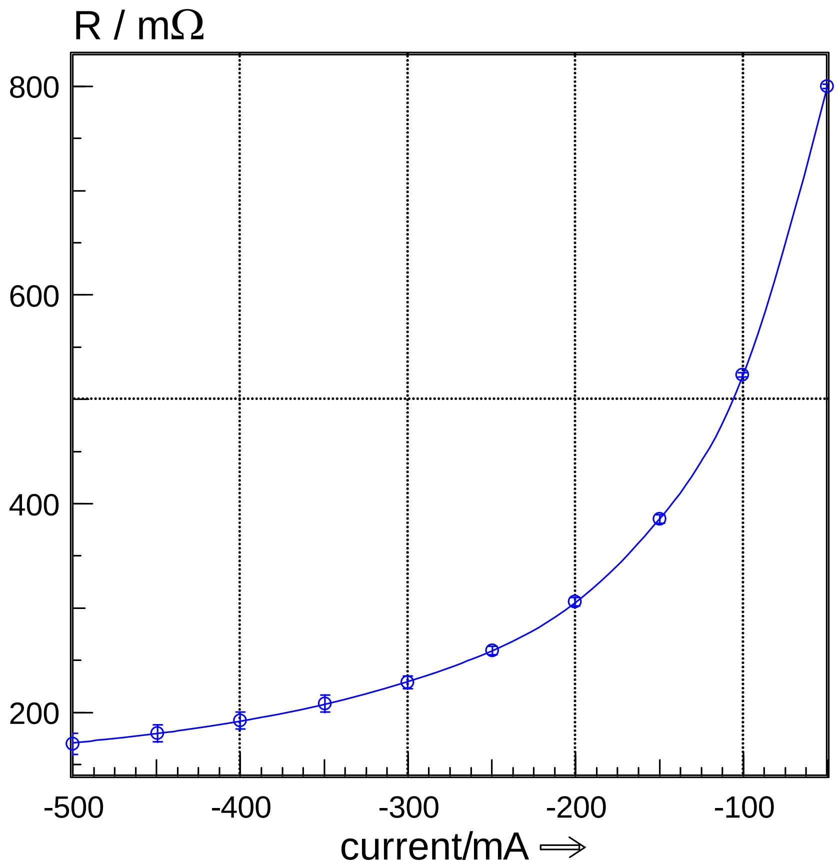


Impedance Measurements during Oxygen Reduction Reaction (ORR) in 10 N NaOH, on Silver Electrodes at Different Current Densities

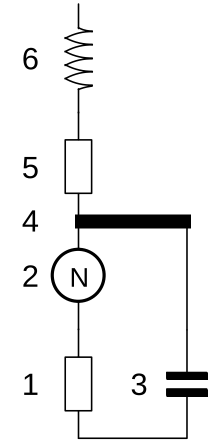




Evaluation of EIS measured during ORR
Equivalent circuit and $R_{ct} = f(i)$



1	170.8	mΩ
2	5.521	$m\Omega \cdot s^{-1/2}$
	19.38	s^{-1}
3	61.37	mF^{α}
	942.8	m
4	1	
	309.9	mΩ
	3.18	mΩ
5	508.6	mΩ
6	73.35	nH



Outlook

- Further improvement of porous electrode models
- Combination and extension of existent and new models
- Application of EIS to segmented cells
- Experimental validation of models using
  - PEFC and DMFC electrodes with different porous structure
  - Gas Diffusion Electrodes (GDE) for Oxygen Consumption Reaction (OCR) in alkaline solution using different gas compositions

Experimental EIS set-up for stack measurements